

VISIT...

LANZAROTE
Caliente.COM

MENDELEVium

[7440-11-1]

Symbol: Md; atomic number 101; atomic weight (most stable isotope) 257; a man-made radioactive transuranium element; an inner-transition element of actinide series; electron configuration [Rn]5f¹³7s²; valence +2, +3. Isotopes, half-lives and their decay modes are:

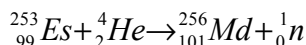
Mass	Half-life	Decay Mode
Md-252	8 min	Orbital electron capture
Md-255	30 min	Orbital electron capture
Md-256	1.5 hr.	Orbital electron capture Alpha decay
Md-257	3.0 hr.	Orbital electron capture Alpha decay
Md-258	60 day	Alpha decay

History

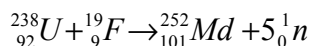
The element first was made by Ghiorso, Harvey, Choppin, Thompson, and Seaborg in 1955 in Berkeley, California. It was synthesized by bombardment of einsteinium-253 with alpha particles of 41 MeV energy in a 60-inch cyclotron. The element was named Mendelevium in honor of Russian chemist Dimitri Mendeleev. Mendelevium -258 isotope with a half-life of 60 days was discovered in 1967. The element has no commercial use except in research to synthesize isotopes of other transuranium elements.

Synthesis

Mendelevium was synthesized first by bombarding Einstein-253 with helium ions. The nuclear reaction is:



All isotopes of medeleium have been synthesized by other nuclear reactions since its discovery. They are prepared by bombarding uranium, einsteinium, and californium isotopes with heavy ions, such as boron-11, carbon-12 and carbon-13.



For example, uranium-238 when bombarded with fluorine-19 produced Md-252. Also, certain nuclear reactions carried out by heavy ion projectiles involve 'stripping' reactions in which some protons and neutrons may transfer from the projectiles onto the target nucleus, but the latter might not capture the projectile heavy ion.

MERCURY

[7439-97-6]

Symbol: Hg; atomic number 80; atomic weight 200.59; a Group IIB (Group 12) element; atomic radius 1.51 Å; ionic radius, $\text{Hg}^{2+}(\text{CN}6)$ 1.16 Å; electron configuration $[\text{Xe}]4f^{14}5d^{10}6s^2$; valence +1 and +2; ionization potential 10.437 eV(1st) and 18.756 eV (2nd); natural isotopes Hg-202 (29.80%), Hg-200 (23.13%), Hg-199 (16.84%), Hg-201 (13.22%), Hg-198 (10.02%), Hg-204 (6.85%), Hg-196 (0.146%); several radioisotopes in the mass range from 189 to 206 are known. Antiquated names: quicksilver; hydrargyrum

History, Occurrence, and Uses

Although mercury is known from early times and was used by alchemists, its first modern scientific applications date back to 1643 when Torricelli used it in the barometer to measure pressure and about eight decades later Fahrenheit used it in the thermometer to measure temperature. Before this, mercury's use was confined to decorative work, gold extraction and medicines. The element was named after the planet mercury and its symbol Hg is taken from the Latin word *hydrargyrum*, which means liquid silver.

The element does not occur in nature in native form. Its principal mineral is cinnabar, the red mercuric sulfide, HgS . Black mercuric sulfide, metacinnabar, also is found in nature. Other ores are livingstonite, HgSb_4S_7 ; coloradite, HgTe ; tiemannite, HgSe ; and calomel, HgCl_2 . Its concentration in the earth's crust is estimated to be 0.08 mg/kg. The average concentration in sea water is about 0.03 µg/L.

Some of the most important uses of mercury are in the electrical and electrolytic applications. A broad range of such applications include mercury batteries and cells in portable radios, microphones, cameras, hearing aids, watches, smoke alarms, and wiring and switching devices. Other notable applications are in mercury vapor lamps, fluorescent tubes and electrical discharge tubes. Mercury electrodes are widely used in electrolytic cells. Mercury cathodes are employed in the electrolysis of sodium chloride to produce caustic soda and chlorine. Another major use, as mentioned earlier, is in thermometers, manometers, barometers and other pressure-sensing devices. Mercury also is used as a catalyst in making urethane foams and vinyl chloride monomers. Mercury and its compounds long have been used as fungicides in paints and in agriculture. Mercury compounds are used in medicines, pigments and analytical reagents.

Physical Properties

Heavy silvery-white liquid; does not wet glass; forms tiny globules; the only metal that occurs at ordinary temperatures as a liquid and one of the two liquid elements at ambient temperatures (the other one being bromine); density 13.534 g/cm³; solidifies at -38.83°C; vaporizes at 356.73°C; vapor pressure 0.015 torr at 50°C, 0.278 torr at 100°C and 17.29 torr at 200°C; critical temperature 1,477°C; critical pressure 732 atm; critical volume 43cm³/mol; resistivity 95.8x10⁻⁶ ohm/cm at 20°C; surface tension 485.5 dynes/cm at 25°C; vis-

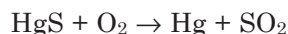
cosity 1.55 centipoise at 20°C.

Thermochemical Properties

ΔH_f° (liq)	0.0
ΔH_f° (gas)	14.68 kcal/mol
ΔG_f° (gas)	7.60 kcal/mol
S° (liq)	18.14 cal/degree mol
S° (gas)	41.82 cal/degree mol
C_p (liq)	6.69 cal/degree mol
C_p (gas)	4.97 cal/degree mol
ΔH_{vap}	14.1 kcal/mol
ΔH_{fus}	0.547 kcal/mol

Production

Mercury mostly is obtained from its sulfide ore, cinnabar. The process involves roasting cinnabar in a furnace between 600 to 700°C. Mercury vapors are cooled and condensed into metal:



Mercury may also be extracted from cinnabar by reduction of the ore with lime at elevated temperature:



Smaller quantities of metal are recovered from mercury-containing industrial and municipal wastes, such as amalgams and batteries. The scrap material is heated in a retort and the vapors of mercury are condensed into high-purity metal.

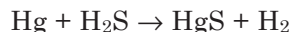
Reactions

Mercury is stable to dry air or oxygen at ordinary temperatures. However, in the presence of moisture, oxygen slowly attacks the metal forming red mercury(II) oxide. Also, when the metal is heated in air or oxygen at about 350°C it is gradually converted to its oxide. The oxide, however, dissociates back to its elements at 440°C.



Mercury readily combines with halogens at ordinary temperatures forming mercury(II) halides.

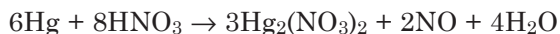
The metal reacts with hydrogen sulfide at room temperature, producing mercury(II) sulfide:



Mercury metal forms both mercury(I) and mercury(II) salts. Oxidizing acids in excess amounts and under hot conditions yields mercury(II) salts. Thus, heating mercury with concentrated nitric or sulfuric acid yields mercury(II) nitrate or mercury(II) sulfate:

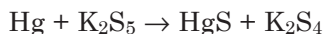


On the other hand, such acids under cold conditions and in limited amounts yield mercury(I) nitrate or mercury(I) sulfate:



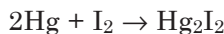
Dilute sulfuric acid has no effect on the metal nor does air-free hydrochloric acid. But dilute nitric acid dissolves the metal; excess mercury in cold dilute acid yields mercury(I) nitrate, the dihydrate $\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ separating out on crystallization. Mercury dissolves in aqua regia forming mercury(II) nitrate.

When mercury is rubbed with powdered sulfur or mixed with molten sulfur, black mercury(II) sulfide is formed. When heated with an aqueous solution of potassium pentasulfide, mercury(II) sulfide is obtained as a scarlet product, known as vermilion and used as an artist's pigment.

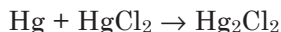


The product on exposure to light gradually converts to black mercury(II) sulfide.

When mercury is rubbed with iodine in the presence of a little ethanol, green mercury(I) iodide forms:



When the metal is intimately mixed with mercury(II) chloride and heated, mercury(I) chloride is obtained:



Mercury does not react with phosphorus but simply dissolves in molten phosphorus.

Water has no effect on mercury, nor does molecular hydrogen. However, atomic hydrogen readily combines with mercury vapors forming hydride, when exposed to radiation from a mercury arc.

Mercury catalytically decomposes hydrogen peroxide. In the presence of acetic acid, the above reaction yields mercury(II) acetate. Mercury reacts with several metals forming their amalgams. Such reactions are exothermic and in the presence of air ignition can occur. The intermetallic compounds obtained

from such amalgamation have varying compositions, such as NaHg, NaHg₂, NaHg₄, Na₃Hg and Na₃Hg₂, etc.

Analysis

Mercury is most accurately determined by the cold vapor atomic absorption spectroscopic method. The instrument is set at the wavelength 253.7 nm. The metal, its salts and organic derivatives in aqueous solution can be measured by this method. The solution or the solid compounds are digested with nitric acid to convert into water-soluble mercury(II) nitrate, followed by treatment with potassium permanganate and potassium persulfate under careful heating. The excess oxidants in the solution are reduced with NaCl-hydroxylamine sulfate. The solution is treated with stannous chloride and aerated. The cold Hg vapor volatilizes into the absorption cell where absorbance is measured.

Mercury and its compounds may also be determined by ICP/AES. The method, however, is less sensitive than the cold vapor-AA technique. The metal also can be measured at low ppb level by colorimetry. Mercury ions react with dithizone in chloroform to show an orange color. Absorbance is measured at 492 nm using a spectrophotometer.

Toxicity

Elemental mercury and all its compounds are highly toxic by all routes of exposure. The element has significant vapor pressure at ambient temperatures (0.0018 torr at 25°C) that can produce severe inhalation hazard. The symptoms from short exposure to high concentration of mercury vapors are bronchitis, coughing, chest pain, respiratory distress, salivation and diarrhea (Patnaik, P. 1999. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 2nd ed., New York: John Wiley and Sons). Other symptoms are tremor, insomnia and depression. Mercury can cause damage to kidney, liver, lungs and brain. Organomercury compounds and inorganic salt solutions can be absorbed into the body through skin contact and cause severe poisoning. It accumulates as Hg²⁺ in the brain and kidneys. US EPA has classified mercury as one of the priority pollutant metals in environmental matrices.

MERCURY(II) ACETATE

[631-60-7]

Formula: Hg(C₂H₃O₂)₂; MW 519.27

Synonym: mercuric acetate

Uses

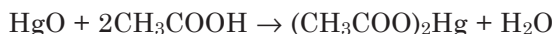
Mercury(II) acetate is the starting material to prepare many organomercuric compounds.

Physical Properties

Colorless crystals; faint vinegar odor; melts at about 178°C; decomposes at higher temperature or when heated rapidly; soluble in water; the solution decomposes on standing producing a yellow precipitate; soluble in alcohol.

Preparation

Mercury(II) acetate is prepared by dissolving mercury(II) oxide in slight excess of warm 20% acetic acid:

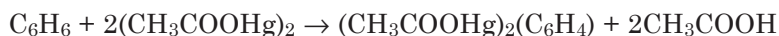


Alternatively, the compound may be made by reacting mercury metal with peracetic acid or hydrogen peroxide (50%) dissolved in acetic acid under careful temperature control.

Reactions

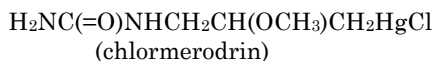
Mercury(II) acetate is the starting material to prepare many organomercury compounds for paints and medicinal use. Such mercuration reactions of organics are discussed briefly below.

Refluxing a mixture of mercury(II) acetate and acetic acid in excess benzene yields phenylmercuric acetate (PMA).

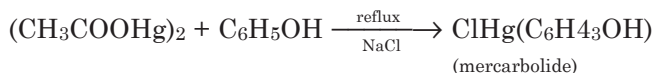


Mercury(II) acetate in acetic acid reacts with allyl chloride and methanol to produce 3-chloro-2-methoxypropyl mercuric acetate, $\text{ClCH}_2\text{CH}(\text{OCH}_3)\text{-CH}_2\text{HgOC(=O)CH}_3$. The compound is difficult to isolate from the solution and generally an ammoniacal solution is used for commercial applications.

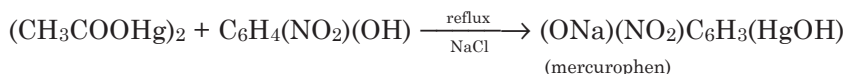
Reaction with allyl urea and methanol, followed by dilution with water and treatment with sodium chloride, precipitates methoxy(urea)propylmercuric chloride, also known as chloromerodrin, a diuretic agent.



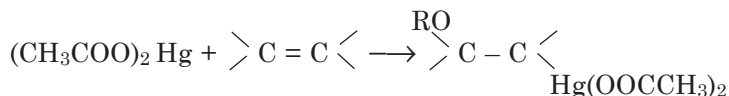
When a mixture of mercury(II) acetate and acetic acid is refluxed with a large excess of phenol and the solution mixture is treated with sodium chloride, a white crystalline product, o-chloromercuriphenol, also known as mercurbolide, precipitates:



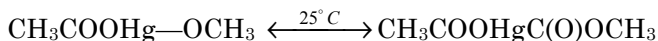
Similarly, refluxing a mixture of mercury(II) acetate and acetic acid with *o*-nitrophenol followed by treatment with sodium chloride yields mercurophen:



In general, reactions with olefins carried out in alcohols yield oxomercuriation products:



A reversible reaction occurs with carbon monoxide at ordinary temperatures in which CO inserts into Hg—O bond of mercury(II) acetate:



Reaction with mercury(II) chloride produces methyl mercury chloride:



The above reaction proceeds via a transition cyclic intermediate.

Reactions with certain metal halides yield their partial methylation products:



Analysis

Elemental composition: Hg 62.95%, C 15.07%, H 1.90%, O 20.07%. The compound is analyzed in aqueous phase by cold vapor-AA or ICP/AES method (See Mercury). It also may be derivatized with an olefin or benzene in alcohol to yield the corresponding "mercuriation" product that may be identified from physical and spectral properties and elemental analysis. An ether or alcoholic solution of the compound may be analyzed by GC/MS. The characteristic masses should be 259, 257, 256, 202, and 200.

Toxicity

A highly poisonous substance by ingestion, intravenous, intraperitoneal and subcutaneous routes and low-to-moderate toxicity by dermal route. An oral LD₅₀ in rats is about 40 mg/kg.

MERCURY(I) CHLORIDE

[10112-91-1]

Formula: Hg_2Cl_2 ; MW 472.09

Synonyms: mercurous chloride; calomel

Uses

Mercury(I) chloride is used in calomel electrodes; in ceramic painting; as a fungicide; in pyrotechnics for producing dark green light; in agriculture for controlling root maggots; and as an antiseptic and antisiphilitic agent in medicine.

Physical Properties

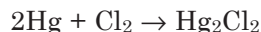
White tetragonal crystals; refractive index 1.973; hardness 1.5 Mohs; density 7.16 g/cm³; does not have a normal melting point; triple point 525°C; sublimes at 383°C; insoluble in water, ethanol and ether.

Thermochemical Properties

ΔH_f°	-63.43 kcal/mol
ΔG_f°	-50.36 kcal/mol
S°	45.79 cal/degree mol

Preparation

Mercury(I) chloride is prepared by passing a limited amount of chlorine gas over mercury in a heated silica retort. Excess chlorine should be avoided as it can oxidize mercury(I) chloride to mercury(II) chloride.

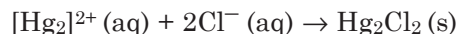


The product generally contains some mercury(II) chloride which is removed by treating the product mixture with water and filtering out the insoluble mercury(I) salt from the soluble mercury(II) salt.

The compound also can be made by heating mercury(II) chloride with mercury. The product Hg_2Cl_2 sublimes and is collected:



Mercury(I) chloride is obtained as a white precipitate by adding a cold acidic solution of sodium chloride or other soluble chloride to a solution of mercurous salt, such as mercury(I) nitrate:

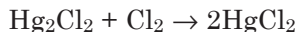


The precipitation method, however, does not form high-purity product as it contains small amounts of reactant and product ions that stick to the Hg_2Cl_2

precipitate and are difficult to remove by washing with water.

Reactions

Mercury(I) chloride oxidizes to mercury(II) chloride when heated with chlorine:



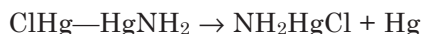
Mercury(I) chloride is a reducing agent and, therefore, its reaction with oxidizing substances can oxidize it to Hg(II) compounds.

When heated at elevated temperatures, it partially dissociates to mercury metal and mercury(II) chloride:



This disproportionation (or breakdown of a compound into two products containing the same element but in different oxidation states) also occurs to some degree when mercury(I) chloride is heated and sublimed in an open container.

Reaction with ammonia in solution forms an unstable black adduct which slowly converts to mercury(II) amidochloride, NH_2HgCl , releasing mercury:



Analysis

Elemental composition: Hg 84.98%, Cl 15.02%

Mercury(I) chloride may be identified from its physical properties, its reaction with ammonia to form a black product, and it may be measured quantitatively for mercury by cold vapor-AA or ICP/AES.

Toxicity

Mercury(I) chloride is highly toxic by ingestion and other routes of exposure. The symptoms include nausea, vomiting, abdominal pain, diarrhea and kidney damage.

MERCURY(II) CHLORIDE

[7487-94-7]

Formula: HgCl_2 ; MW 271.50; covalent bonding, slightly ionized in water

Synonyms: mercuric chloride; mercury bichloride; corrosive sublimate; mercury perchloride

Uses

Mercury(II) chloride is used in dry batteries; in electroplating aluminum;

for extracting gold; in etching steel; for preserving wood; for tanning leather; in photographic solution; in fabric printing; as an agricultural fungicide; as a disinfectant; and topical antiseptic. The compound also is used as an intermediate in organic syntheses; as a reagent in analytical chemistry; and as a catalyst in the preparation of mercury(II) chloride. A major application of mercury(II) chloride involves preparing several other mercury compounds.

Physical Properties

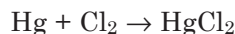
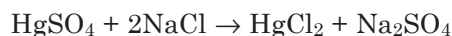
White orthogonal crystal; density 5.6 g/cm³; melts at 276°C; vaporizes at 304°C; vapor pressure 5 torr at 166°C and 60 torr at 222°C (the substance is in the solid state at these temperatures); critical temperature 700°C; critical volume 174 cm³/mol; moderately soluble in water (7.4 g/100 mL at 20°C), solubility increases in the presence of HCl or Cl⁻ ion in the solution; pH of 0.2M solution 3.2; soluble in alcohol, ether, acetone and ethyl acetate; slightly soluble in benzene and carbon disulfide.

Thermochemical Properties

ΔH_f°	-53.6 kcal/mol
ΔG_f°	-42.7 kcal/mol
S°	34.9 cal/degree mol

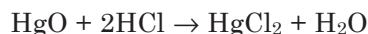
Preparation

Mercury(II) chloride, like mercury(I) chloride, is most conveniently made by dry methods that involve either heating a mixture of mercury(II) sulfate and sodium chloride or heating mercury metal with excess chlorine:



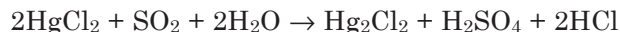
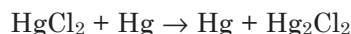
The product HgCl₂ is sublimed off and collected as a white transparent crystalline mass. Very pure product is obtained in these reactions. Excess chlorine in the latter reaction is removed by absorption over sodium hydroxide.

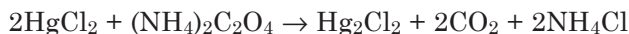
The wet method of preparation involves treating mercury(II) oxide with hydrochloric acid followed by evaporation of the solution and crystallization:



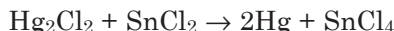
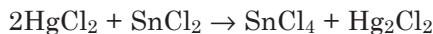
Reactions

Mercury(II) chloride is reduced to mercury(I) chloride by heating with mercury; or by treatment with sulfur dioxide, tin(II) chloride, ammonium oxalate and other reducing agents in aqueous solutions:





Reaction with tin(II) chloride first forms a white precipitate of mercury(I) chloride which then is further reduced to give a black deposit of mercury:



Mercury(II) chloride is a weakly dissociated salt. When hydrogen sulfide is slowly passed into its solution, a pale yellow precipitate due to $\text{HgCl}_2 \cdot 2\text{HgS}$ is first formed, which on further treatment with H_2S converts to black amorphous HgS :

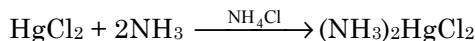


Reaction with alkali hydroxides gives a yellow precipitate of mercury(II) oxide, HgO .

When aqueous ammonia is added to mercury(II) chloride, a white precipitate, the so-called “infusible” white precipitate of composition NH_2HgCl forms:



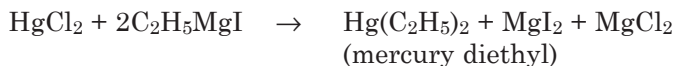
The product decomposes on sublimation forming mercury(II) chloride, ammonia, and nitrogen. However, in the presence of ammonium chloride, the same reaction with ammonia with HgCl_2 in aqueous solution yields “fusible” white precipitate, $(\text{NH}_3)_2\text{HgCl}_2$. Similar product also is obtained by reaction of gaseous ammonia with solid mercury(II) chloride. However, the solid mercury(II) chloride is more stable than the above “infusible” product and can be melted without decomposition.



Mercury(II) chloride reacts with alkali metal chlorides to form water soluble complex salts, such as KHgCl_3 or K_2HgCl_4 :



Action of Grignard reagent on mercury(II) chloride yields mercury alkyls:



Analysis

Elemental composition: Hg 73.88%, Cl 26.12%. In an aqueous solution of

the salt, mercury may be analyzed by cold vapor–AA technique and chloride measured by ion chromatography.

Toxicity

The compound is a systemic poison by ingestion, skin contact and other routes of exposure. It may produce adverse teratogenic and reproductive effects. There is limited evidence of carcinogenicity in experimental animals.

LD₅₀ oral (rat): 1mg/kg

MERCURY(II) CYANIDE

[592-04-1]

Formula: Hg(CN)₂; MW 252.63

Synonym: mercuric cyanide

Uses

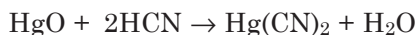
Mercury(II) cyanide is a topical antiseptic.

Physical Properties

Colorless tetragonal crystal; density 4.0 g/cm³; decomposes at 320°C; soluble in water and ethanol; slightly soluble in ether.

Preparation

Mercury(II) cyanide is prepared by the action of mercury(II) oxide on aqueous hydrocyanic acid, followed by evaporation:



Alternatively, it is produced by the reaction of alkali cyanides with a mercury(II) salt solution.

Analysis

Elemental composition: Hg 79.40%, C 9.51%, N 11.09%. Aqueous solution is analyzed for mercury metal by AA–cold vapor techniques or by ICP/AES (see Mercury). The cyanide ion may be measured by cyanide ion-specific electrode or by ion chromatography after appropriate dilution.

MERCURY DIMETHYL

[593-74-8]

Formula: (CH₃)₂Hg; MW 230.67; covalent bonding of methyl radicals to mercury atom; linear shape

Synonyms: dimethylmercury; methylmercury

Occurrence and Uses

Mercury dimethyl is a toxic environmental pollutant. It is found in polluted bottom sediments and in the bodies of fishes and birds. In the bodies of fishes and birds it occurs along with monomethyl mercury. The latter, as CH_3Hg^+ ion, is formed by microorganism-induced biological methylation of elemental mercury or agricultural fungicide mercury compounds that are discharged into the environment.

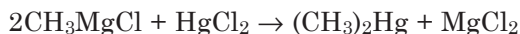
Mercury dimethyl is used in inorganic synthesis; and as a reference standard for Hg-NMR.

Physical Properties

Colorless liquid; sweet faint odor; refractive index 1.5452; flammable; volatile; density 3.19 g/mL at 20°C; boils at 94°C; solidifies at -43°C; insoluble in water; soluble in ether and alcohols.

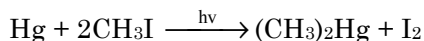
Preparation

Mercury alkyls are readily obtained by the actions of Grignard reagents (magnesium alkyl halides) on mercury(II) chloride. Thus, mercury dimethyl is made from magnesium methyl chloride and mercury(II) chloride:



The above reaction proceeds through the formation of mercury methyl chloride as an intermediate (not shown above).

Alternatively, the compound can be prepared by the reaction of mercury with methyl iodide in the presence of sunlight; or by “mercuration” reaction of organics.

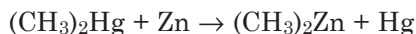


Reactions

Mercury dimethyl, unlike zinc dimethyl, is fairly stable at ordinary temperatures, and is not attacked by air or water.

Mercury dimethyl undergoes single replacement reactions with several metals such as alkali and alkaline earth metals, zinc, aluminum, tin, lead and bismuth forming their corresponding dialkyls.

Such reaction is a synthetic route to prepare many organometallic compounds. Thus, reaction with metallic zinc yields zinc dimethyl:



Analysis

Elemental composition: 86.96%, C 10.41%, H 2.62%. The compound can be identified from its physical properties, elemental analyses and infrared spectra. Mercury can be identified by cold-vapor AA or ICP/AES after cautious extraction with nitric acid. In a suitable organic solvent, it may be analyzed by GC/MS. The characteristic ions are 217, 215, 202, 200, 232 and 230.

Toxicity

Mercury dimethyl is a highly toxic substance by all routes of exposure. Several cases of human poisoning are well documented. (Patnaik, P. 1999. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 2nd ed. p. 574, New York: John Wiley & Sons.) The compound can accumulate in the brain and blood of humans. Intake of small quantities can cause death.

MERCURY FULMINATE

[628-86-4]

Formula: $\text{Hg}(\text{CNO})_2$; MW 284.63

Synonyms: mercury(II) cyanate; fulminate of mercury

Uses

Mercury fulminate is used in explosives to initiate boosters.

Physical Properties

White or grayish cubic crystals; density 4.42 g/cm³; explodes on heating; slightly soluble in water; soluble in ethanol and ammonia solution.

Preparation

Mercury fulminate is prepared by the reaction of mercury metal with strong nitric acid and ethanol. The preparative method involves pouring a nitric acid solution of mercury(II) nitrate into ethanol. The reaction is not well understood.

Hazard

The compound is highly sensitive to heat and impact. It detonates when heated at 180°C or struck hard. It also is a toxic substance exhibiting the symptoms of mercury poisoning.

MERCURY(II) IODIDE

[7774-29-0]

Formula: HgI_2 ; MW 454.40

Synonym: mercuric iodide

Uses

Mercury(II) iodide is used as an analytical reagent, in Nessler's reagent for the analysis of ammonia. The compound also is used in ointments for the treatment of skin diseases.

Physical Properties

Exists in two allotropic forms: red tetragonal allotropic modification (alpha form) and the yellow rhombic modification (beta form).

The red iodide has a density 6.36 g/cm³ at 25°C; transforms to yellow form at 127°C; also converts to yellow form at -180°C; slightly soluble in water (100 mg/L at 25°C); moderately soluble in acetone and alcohol.

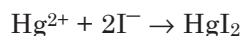
The yellow iodide has a density of 6.09 g/cm³ at 27°C; melts at 259°C; vaporizes at 354°C; practically insoluble in water; low-to-moderately soluble in alcohol, benzene and other organic solvents.

Thermochemical Properties

ΔH_f° (red)	-25.2 kcal/mol
ΔH_f° (yellow)	-24.6 kcal/mol
ΔG_f° (red)	-24.3 kcal/mol
S° (red)	43.0 cal/degree mol

Preparation

Mercury(II) iodide is precipitated in its yellow form by adding a stoichiometric amount of potassium iodide to an aqueous solution of mercury(II) salt (e.g., HgCl₂):

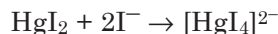


The yellow precipitate rapidly turns red and dissolves in solution when excess potassium iodide is added.

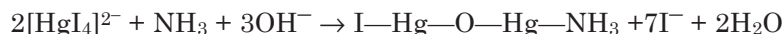
Also, mercury (II) iodide is formed when mercury is rubbed with iodine moistened with ethanol.

Reactions

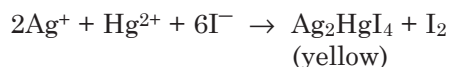
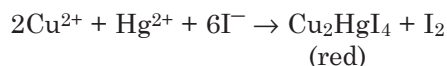
Mercury(II) iodide reacts with excess iodide ion forming complex tetraiodomercurate(II) ion, [HgI₄]²⁻:



In caustic soda or caustic potash solution, mercury(II) iodide forms complex salts, Na₂HgI₄ and K₂HgI₄, respectively. Alkaline solution of this complex in excess potassium hydroxide is known as Nessler's reagent, used to analyze ammonia. The reaction of Nessler's reagent with ammonia may be written as:



Similar complexes of silver, copper and other metals are known. Some of them change colors on heating and are used in heat-sensitive paints and applied to machine parts made out of brass or iron:



In general, mercury(II) iodide forms neutral complexes of compositions $M_2(HgI_4)$ and $M(HgI_3)$ with alkali and alkaline metal iodides.

When heated with dilute caustic potash solution, a yellow brown powder of composition $HgI_2 \cdot 3HgO$ is obtained.

MERCURY(I) NITRATE

Formula: $Hg_2(NO_3)_2$; MW 525.19; exists as dihydrate, $Hg_2(NO_3)_2 \cdot 2H_2O$ [7782-86-7]

Synonym: mercurous nitrate

Uses

Mercury(I) nitrate is used for preparing calomel and other mercury(I) salts. Other applications are fire gilding and blackening of brass.

Physical Properties

The dihydrate is colorless crystalline substance (the anhydrous salt consists of white monoclinic crystals); density 4.8 g/cm³; melts at 70°C with partial decomposition; soluble in water (hydrolyzes); soluble in cold dilute nitric acid.

Preparation

Mercury(I) nitrate is prepared by action of metallic mercury with moderately dilute nitric acid. Excess mercury should be used to prevent the formation of mercury(II) nitrate. Hot or concentrated acid must be avoided as it yields the mercury(II) salt.

It also is formed by the reaction of mercury with mercury(II) nitrate solution.

Reactions

Mercury(I) nitrate is acidic in solution. Its aqueous solution hydrolyzes on standing forming a yellow precipitate of the basic nitrate, $Hg_2(NO_3)(OH)$. This precipitation occurs more rapidly when diluted with water and warmed. Sufficient nitric acid in the solution suppresses hydrolysis.

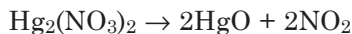
However, if the solution is boiled, mercury(I) nitrate disproportionates to mercury(II) nitrate and mercury:



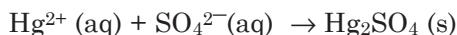
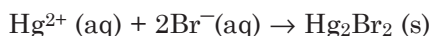
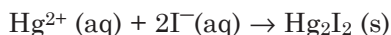
Also, such disproportionation occurs due to light.

Mercury(I) nitrate exhibits reducing properties. It is partially oxidized by atmospheric oxygen at ambient temperatures, forming mercury(II) nitrate and mercury.

On gentle heating, the solid salt yields mercury(II) oxide and nitrogen dioxide:



Mercury(I) nitrate undergoes double decomposition reactions with anions in aqueous solution, forming corresponding mercury(I) salts. With potassium iodide and sodium bromide, yellow mercury(I) iodide and white mercury(I) bromide precipitate, respectively. Similarly, mercury(I) nitrate in acid medium reacts with dilute sulfuric acid to form mercury(I) sulfate:



Analysis

Elemental composition: Hg 76.39%, N 5.33%, O 18.28%. The salt is dissolved in dilute nitric acid and analyzed for mercury (see Mercury). The compound is blackened by ammonia and caustic alkali solutions. It may be identified by physical and x-ray properties.

Toxicity

Poison by ingestion and other routes of exposure.

MERCURY(II) NITRATE

[10045-94-0]

Formula: $\text{Hg}(\text{NO}_3)_2$; MW 324.60; occurs as monohydrate, $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ [7783-34-8], and dihydrate, $\text{Hg}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$.

Synonym: mercuric nitrate

Uses

Mercury(II) nitrate is used in the preparation of other mercury compounds; in organic synthesis; and as an analytical standard for mercury.

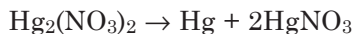
Physical Properties

The monohydrate is a white crystalline or powdery substance; density 4.3g/cm³; decomposes on heating; soluble in water and nitric acid; insoluble in alcohol.

Preparation

Mercury(II) nitrate is prepared by dissolving mercury in excess hot concentrated nitric acid. Upon evaporation of the solution, large colorless deliquescent crystals of monohydrate, $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, form.

It also is obtained by boiling a solution of mercury(I) nitrate or by the action of light on mercury(I) nitrate:



Reactions

Gentle heating of mercury(II) nitrate gives mercury(II) oxide evolving nitrogen and oxygen:



However, on strong heating, mercury nitrate decomposes to mercury metal:



When excess alkali hydroxide is added to a solution of mercury(II) nitrate, a yellow precipitate of HgO is obtained.

Addition of potassium thiocyanate solution forms a white precipitate of mercury(II) thiocyanate:



Addition of a small amount of alkali iodide to mercury(II) nitrate solution precipitates mercury(II) iodide:



Similarly, mercury(II) cyanide precipitates upon the addition of potassium cyanide to mercury(II) nitrate solution:



Analysis

Elemental composition: Hg 61.80%, N 8.63%, O 29.57%. The compound dissolved in dilute hydrochloric acid and the solution diluted appropriately and analyzed for mercury by cold vapor-AA technique. The aqueous solution is analyzed for nitrate ion by nitrate ion-specific electrode or by ion chromatography.

Toxicity

Mercury(II) nitrate is highly toxic by ingestion and possibly other routes of exposure. The LD₅₀ oral for the dihydrate in mouse is 25 mg/kg.

MERCURY(II) OXIDE

[21908-53-2]

Formula: HgO; MW 216.59

Synonym: mercuric oxide

Occurrence and Uses

Mercury(II) oxide is found natively in the mineral montroydite. The oxide is used primarily to prepare other mercury salts. The red form of the oxide is used as a depolarizer in a certain type of dry batteries. Other applications are paints and pigments; as a reagent in several wet analyses; and to catalyze in organic reactions. The oxide also is used in ointments as a topical antiseptic.

Physical Properties

Mercury(II) oxide exists in two modifications, red and yellow, differing in particle size—finer particles under $5\mu\text{m}$ appear red, while particle size greater than $8\mu\text{m}$ appear reddish. The yellow form converts to red oxide on heating, which reverts back to yellow oxide on cooling. At 400°C , the red oxide becomes black which changes back to red again on cooling. The oxide decomposes at 500°C .

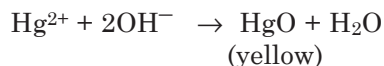
Orthogonal crystalline powder; refractive index (for montroydite) 2.37; density 11.14 g/cm^3 ; Moh's hardness 2.5; insoluble in water and ethanol; soluble in dilute acids and aqueous solutions of alkali iodides and cyanides.

Thermochemical Properties (Red Modification)

ΔH_f°	-21.70 kcal/mol
ΔG_f°	-13.98 kcal/mol
S°	$16.80\text{ cal/degree mol}$
C_p	$10.54\text{ cal/degree mol}$

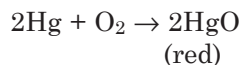
Preparation

Yellow mercury(II) oxide is precipitated upon the addition of excess caustic soda or caustic potash to an aqueous solution of mercury(II) nitrate or chloride:

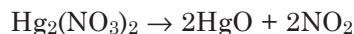


Most precipitation methods give yellow mercury(II) oxide. However, if barium hydroxide is added to a hot solution of mercury(II) nitrate, the product is red oxide.

Red mercury(II) oxide is obtained by heating mercury in air or oxygen (preferably under pressure) at 450°C :



or by thermal decomposition of mercury(II) nitrate or mercury(I) nitrate:



or by boiling the yellow oxide in a solution of sodium or potassium chloride.

Mercury(II) oxide also is obtained as an intermediate when cinnabar (HgS)

is roasted in air in the extraction of mercury.

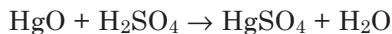
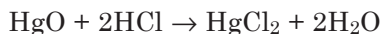
Reactions

The yellow form of the HgO is more reactive than the red form due to finer particle size.

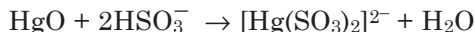
When heated at 500°C, mercury(II) oxide decomposes to its elements:



Mercury(II) oxide is a basic oxide. It reacts with acids forming their mercury(II) salts:

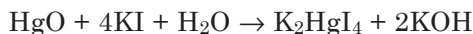


Mercury(II) oxide dissolves in neutral sodium or potassium sulfite solution forming sulfitomercurate(II) ion:

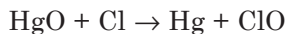


Upon evaporation of the solution, complex salt crystals such as $\text{Na}_2[\text{Hg}(\text{SO}_3)_2]$ or $\text{K}_2[\text{Hg}(\text{SO}_3)_2]$ form.

Mercury(II) oxide reacts with potassium iodide in solution, forming potassium tetraiodomercurate(II):



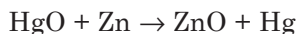
Reaction with chlorine yields chlorine monoxide, ClO, and in aqueous solution or with chlorine water, the product is hypochlorous acid, HOCl:



The oxide is reduced to mercury metal when heated with mercury(II) sulfide:



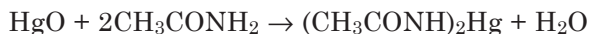
Similarly, reaction with zinc and other reducing agents converts the oxide to metallic mercury:



Mercury(II) oxide dissolves in a saturated solution of mercury(II) cyanide, forming mercury oxycyanide, $\text{Hg}(\text{CN})_2 \cdot \text{HgO}$.

Mercury(II) oxide dissolves in an aqueous solution of acetamide forming mercury(II) acetamide. In this reaction, mercury replaces both the hydrogen atoms of the amide functional group, forming covalent N—Hg bond:

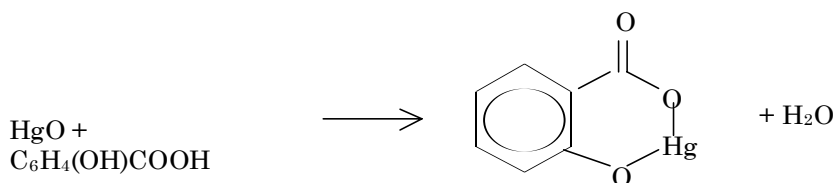
578 MERCURY(II) SULFATE



Similarly, reaction with succinimide yields mercury succinimide [584-43-0].

The yellow oxide reacts with aqueous ammonia to yield a bright yellow crystalline powder, dihydroxymercury(II)-ammonium hydroxide, known as Millon's base, $[(\text{HO}-\text{Hg})_2\text{NH}_2]\text{OH}$ [12529-66-7], a photosensitive unstable product.

Mercury(II) oxide yields mercury(II) salicylate [5970-32-1] when added to an aqueous solution of salicylic acid:



The product was used medicinally for the treatment of syphilis.

Analysis

Elemental composition: Hg 92.61%, O 7.39%. The compound is digested in nitric acid and mercury in an appropriately diluted acid extract and then is measured by cold-vapor AA or by ICP. The compound may be characterized nondestructively by x-ray methods.

Toxicity

It is highly toxic by ingestion and inhalation as dust. Toxic symptoms are those of mercury (see Mercury). The oral LD_{50} in rodents is between 15 to 20 mg/kg.

MERCURY(II) SULFATE

[7783-35-9]

Formula: HgSO_4 ; MW 296.65

Synonym: mercuric sulfate

Uses

Mercury(II) sulfate is an electrolyte for primary batteries. Other applications are in extraction of gold and silver from roasted pyrites; as a catalyst in organic reactions such as conversion of acetylene to acetaldehyde; and as a reagent for wine coloring.

Physical Properties

White monoclinic crystal; hygroscopic; density 6.47 g/cm³; decomposes in water; soluble in hot dilute sulfuric acid, hydrochloric acid and concentrated solution of sodium chloride.

Thermochemical Properties

$$\Delta H_f^\circ \quad -169.1 \text{ kcal/mol}$$

Preparation

Mercury(II) sulfate is prepared by heating mercury with an excess of concentrated sulfuric acid; or by dissolving mercury(II) oxide in concentrated sulfuric acid. The solution is evaporated repeatedly to yield anhydrous salt as white leaflets. However, in the presence of a small amount of water, the monohydrate of the salt, $\text{HgSO}_4 \cdot \text{H}_2\text{O}$ crystallizes as a colorless rhombic prism. Hydrolysis occurs in the presence of a large amount of water, forming a yellow basic sulfate, $\text{HgSO}_4 \cdot 2\text{HgO}$.

The compound also is prepared by treating alkali sulfate, such as sodium or potassium sulfate with a solution of mercury(II) nitrate.

Reactions

Mercury(II) sulfate on heating first turns yellow and then becomes red-brown. When heated to red heat, it decomposes to mercury, sulfur dioxide, and oxygen.



Mercury(II) sulfate hydrolyzes in water forming a basic sulfate $\text{HgSO}_4 \cdot 2\text{HgO}$. It forms double sulfates with alkali metal sulfates, such as $\text{K}_2\text{SO}_4 \cdot 3\text{HgSO}_4 \cdot 2\text{H}_2\text{O}$.

Analysis

Elemental composition: Hg 67.62%, S 10.81%, O 21.57%. The compound is digested in nitric acid and the acid extract may be analyzed by cold vapor AA or ICP/AES. It also may be characterized by x-ray methods.

MERCURY(II) SULFIDE

[1344-48-5]

Formula: HgS ; MW 232.65

Synonyms: mercuric sulfide; cinnabar; vermilion; metacinnabar

Occurrence and Uses

Mercury(II) sulfide occurs in nature as the mineral cinnabar. This is the red sulfide of mercury, which is the principle source of all mercury produced in the world. The black sulfide, known as metacinnabar, occurs rarely in nature, sometimes coexisting with the red form and found as a black deposit over cinnabar.

The most important use of this compound, the principal ore of mercury, is for making mercury metal and its salts. Another major application is pigment. Artificially prepared scarlet product, vermilion, is used as artists' pigment

and for coloring plastics. The red form also is used as an antibacterial agent. The black sulfide is used for coloring horns, rubber, and other materials.

Physical Properties

Mercury(II) sulfide has several modifications, the only two stable allotropic forms are:

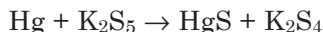
1. the red hexagonal form known as cinnabar (alpha form), and
2. the black cubic modification (beta form).

Cinnabar is a red crystalline or powdery substance; hexagonal crystal system; refractive index 2.854; density 8.10 g/cm³; sublimes at 583.5°C; color changes to brown at 250°C and converts to black sulfide at 386°C; reverts to red color on cooling; insoluble in water, alcohol and nitric acid; soluble in aqua regia and solutions of alkali metal sulfides; decomposed by hot concentrated sulfuric acid.

Black sulfide is a black amorphous powder or crystalline substance (beta form); cubic structure; metastable at ordinary temperatures; converts to red sulfide by sublimation at ordinary pressure; density 7.73 g/cm³; melts at 583.5°C; insoluble in water, alcohol and nitric acid; soluble in aqua regia, alkalis, and solutions of alkali metal sulfides.

Preparation

Red sulfide occurs natively and is mined from mineral cinnabar. Also it can be prepared by heating mercury with a solution of potassium pentasulfide, producing a scarlet cinnabar:



The red sulfide also may be made from black sulfide by heating in a concentrated solution of alkaline polysulfide. The shade of pigment varies with temperature, reaction time, and concentration of the black sulfide.

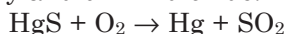
Alternatively, vermilion may be made by grinding sodium sulfide with sulfur and slowly adding mercury. The shades are not bright when prepared at 0°C.

The black mercury(II) sulfide is prepared usually by precipitation from an aqueous solution of mercury(II) salt with hydrogen sulfide. Thus, when H₂S is passed into a solution of HgCl₂, a pale yellow precipitate of composition HgCl₂·2HgS forms. This converts to amorphous black HgS on further treatment with H₂S.

The black sulfide may also be made by other methods such as adding sodium thiosulfate, Na₂S₂O₃ in excess to a dilute solution of sodium mercurichloride, Na₂HgCl₄ and treating mercury with molten or powdered sulfur.

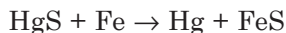
Reactions

When heated in a current of air, mercury(II) sulfide is converted into metallic mercury and sulfur dioxide:



Similar reduction to metallic mercury occurs when the sulfide is heated with

several metals or metal oxides:



Mercury(II) sulfide dissolves in concentrated solutions of alkali or alkaline-earth metal sulfides forming thiosalts, such as $\text{Na}_2[\text{HgS}_2] \cdot x\text{H}_2\text{O}$. Such thiosalts are stable in solution only when alkaline hydroxides are present in excess. These salts also are obtained as bright and deliquescent needles when HgS is heated with sulfur and alkaline hydroxides.

Analysis

Elemental composition: Hg 86.22%, S 13.78%. The compound may be identified from its physical properties and also by x-ray methods. The compound may be heated in a current of air and SO_2 formed may be analyzed by GC-FID or GC-FPD. Mercury(II) sulfide may be digested with aqua regia, diluted appropriately, and analyzed for mercury metal by AA using cold vapor method or by ICP-AES (see Mercury).

MOLYBDENUM

[7439-98-7]

Symbol: Mo; atomic number 42; atomic weight 95.94; a Group VIB (Group 6) transition metal element; atomic radius 1.36Å (coordination number 8); ionic radius 0.92Å and 0.62Å for Mo^{3+} and Mo^{6+} , respectively; atomic volume 9.41 cm^3/mol ; electron configuration $[\text{Kr}]4d^55s^1$; oxidation states 0, +2, +3, +4, +5, and +6; most stable oxidation state +6; seven natural isotopes: Mo-92 (14.84%), Mo-94 (9.25%), Mo-95 (15.92%), Mo-96 (16.68%), Mo-97 (9.55%), Mo-98 (24.13%), Mo-100 (9.63%); several artificial isotopes in the mass range 88-106 are known.

History, Occurrence, and Uses

Molybdenum was first identified as a distinct element by Swedish chemist Karl Wilhelm Scheele in 1778. The metal was isolated by Hjelm in 1782 by reduction of its oxide with carbon. Moissan in 1895 isolated the metal in highly purified form by electrolytic reduction of its oxide and studied many of its physical and chemical properties. The element derived its name in 1816 from the word *molybdos*, meaning a soft mineral that appeared like lead.

Molybdenum does not occur in nature in free elemental form. Its most important ore is molybdenite, MoS_2 , from which the metal is obtained commercially. Other ores are powellite (calcium tungstomolybdate), $\text{Ca}(\text{MoW})\text{O}_4$, and wulfenite (lead molybdate), PbMoO_4 . The metal is an essential nutrient for plants and is found in trace amounts in some plants such as peas and beans, which absorb it from soil. Also, molybdenum is found in many natural petroleum oils.

The largest quantities of molybdenum produced are consumed in the steel industry. The metal is incorporated to steel to impart high resistance and hardness to the steel and to improve its mechanical properties. In the chemical industry, molybdenum compounds are used widely in coloring agents and solid lubricants. Molybdenum compounds are used also as catalysts in many oxidation-reduction reactions and in petroleum refining for production of high-octane gasoline. The metal also is used as the starting material to prepare many of its salts. Important commercial uses of molybdenum compounds are discussed separately under their individual headings.

Physical Properties

Silvery-white metal or grayish-black powder; cubic crystalline structure; density 10.22 g/cm³; melts at 2,623°C; vaporizes at 4,639°C; vapor pressure 1 torr at 2,830°C and 5 torr at 3,120°C; compressibility 3.6x10⁻⁷ cm²/kg at 20°C; electrical resistivity 5, 15, and 32 microhm-cm at 0°C, 400°C and 1,000°C, respectively; insoluble in water.

Thermochemical Properties

ΔH_f° (cry)	0.0
ΔH_f° (gas)	157.3 kcal/mol
ΔG_f° (gas)	146.4 kcal/mol
S° (cry)	6.86 cal/degree mol
S° gas)	43.5 cal/degree mol
C_p (cry)	5.76 cal/degree mol
C_p (gas)	4.97 cal/degree mol
ΔH_{fus}	8.96 kcal/mol
Coeff. of linear expansion	4.8x10 ⁻⁶ /°C
Thermal conductivity (at 27°C)	1.38 W/cmK

Production

Molybdenum is recovered primarily from its sulfide ore, molybdenite, MoS₂. It also is produced, although to a much lesser extent, from the tungsten ore wulfenite, which yields lead molybdate, PbMoO₄. The first phase of the recovery process generally involves concentration of the ore, because ore coming from the mine is very lean and usually contains less than one percent molybdenum. Molybdenite at first is concentrated by flotation which concentrates the MoS₂ over 90%. If wulfenite is used as a source material, concentration is usually done by hydraulic methods.

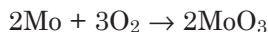
The concentrated molybdenite ore is then roasted in air, converting molybdenum sulfide to molybdenum trioxide MoO₃. This is harvested in high purity by sublimation. An alternative is to leach molybdenite concentrate with dilute ammonia solution, which converts the metal to ammonium molybdate, (NH₄)₂MoO₄. Molybdenum trioxide or ammonium molybdate product is then heated with hydrogen at elevated temperatures from 500 to 1,150°C in a furnace to produce molybdenum powder.

Reactions

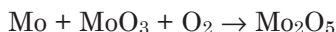
At ordinary temperatures molybdenum metal is fairly stable to air, water and most mineral acids. The metal shows high resistance to HCl, H₂SO₄, HF, H₃PO₄ and most other mineral acids in the absence of any oxidizing agent. However, the metal is attacked by nitric acid and aqua regia. The reaction is rapid with dilute nitric acid but slow with concentrated nitric acid due to the formation of a protective oxide film over the metal. With excess nitric acid, the solution becomes colorless due to formation of molybdic acid, H₂MoO₄. Excess molybdenum turns the solution red. Although no reaction occurs with dilute or concentrated H₂SO₄ at ordinary temperatures, when heated above 110°C molybdenum reduces sulfuric acid to sulfur dioxide:



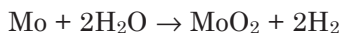
Molybdenum is very stable to oxygen at ambient temperatures. However, when heated in air or oxygen to red heat the metal readily converts to its trioxide, MoO₃:



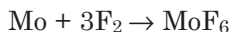
Heating the finely divided metal with its trioxide at 750°C makes molybdenum pentoxide, Mo₂O₅:



When heated in steam at 800°C, the metal is converted to its dioxide, MoO₂:



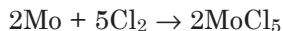
Molybdenum combines with fluorine gas at ordinary temperatures forming colorless hexafluoride, MoF₆:



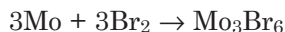
In the presence of oxygen, an oxyfluoride MoOF₄ is obtained:



Reactions with chlorine and bromine occur only at elevated temperatures. With chlorine the product is molybdenum pentachloride:



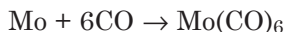
When bromine vapor is passed over molybdenum metal at 600 to 700°C in an atmosphere of nitrogen, the product is trimeric molybdenum dibromide (trimolybdenum hexabromide) (Mo₃Br₆):



Two other bromides are also obtained from the elements. These are molybdenum tribromide, MoBr_3 , and molybdenum tetrabromide, MoBr_4 . MoBr_3 , a black solid, is obtained by heating the elements at 350 to 400°C.

Molybdenum does not react with iodine even at red heat. It combines with carbon at elevated temperatures forming molybdenum carbide, Mo_2C . When molybdenum powder is heated with ammonia gas, two nitrides, Mo_2N and MoN are formed. The metal does not combine readily with nitrogen even at elevated temperature. The above nitrides are obtained only in small yields. The metal has very little affinity for hydrogen even in finely divided state. Finely divided molybdenum absorbs hydrogen only to a very small extent. Hydrogen desorbs completely at 300°C. Molybdenum reacts with sulfur and hydrogen sulfide at elevated temperatures, forming molybdenum disulfide, MoS_2 . The same product also is obtained from hydrogen sulfide alone. The metal combines with tin, zinc, iron and aluminum in molten state.

Finely divided molybdenum reacts with carbon monoxide under pressure to form molybdenum hexacarbonyl:



However, when heated with carbon monoxide at temperatures above 1,000°C, no carbonyl is obtained but a thin film of molybdenum carbide forms over the metal.

Analysis

Molybdenum may be identified at trace concentrations by flame atomic absorption spectrometry using nitrous oxide-acetylene flame. The metal is digested with nitric acid, diluted and analyzed. Aqueous solution of its compounds alternatively may be chelated with 8-hydroxyquinoline, extracted with methyl isobutyl ketone, and analyzed as above. The metal in solution may also be analyzed by ICP/AES at wavelengths 202.03 or 203.84 nm. Other instrumental techniques to measure molybdenum at trace concentrations include x-ray fluorescence, x-ray diffraction, neutron activation, and ICP-mass spectrometry, this last being most sensitive.

MOLYBDIC ACID AND MOLYBDATES

MOLYBDIC ACID

[7782-91-4]

Formula: H_2MoO_4 (or $\text{MoO}_3 \cdot \text{H}_2\text{O}$); MW 161.95; also forms a monohydrate $\text{H}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (or $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$); [13462-95-8], MW 179.97; and a dihydrate, $\text{H}_2\text{MoO}_4 \cdot 3\text{H}_2\text{O}$ (or $\text{MoO}_3 \cdot 3\text{H}_2\text{O}$), MW 197.99.

The monohydrate is a yellow solid consisting of monoclinic crystals; density 3.124 g/cm³ at 15°C; loses water of crystallization on heating at 70°C; sparingly soluble in cold water (1.33 g/L at 18°C); moderately soluble in hot

water 25.68 g/L at 70°C; soluble in caustic soda and sodium carbonate solution.

The anhydrous acid consists of white hexagonal crystals; density 3.112 g/cm³; converts to molybdenum trioxide, MoO₃ at 70°C; slightly soluble in water; soluble in alkalies and sulfuric acid.

The monohydrate is prepared by treating a molybdate solution with nitric acid, followed by crystallization which may take several weeks to separate out as a yellow solid. The anhydrous molybdic acid is obtained as a white crystalline substance by careful dehydration of the yellow monohydrate.

MOLYBDATES

Normal isopoly- and peroxy-molybdates of ammonium and several metals are known. The normal or orthomolybdates may be considered as salts of molybdic acid having formulas H₂MoO₄·xH₂O or M₂O·MoO₃·xH₂O. They are either of monoclinic or scheelite type crystal structure and obtained as hydrated salts.

Normal molybdates are prepared by two methods: (1) precipitating the insoluble metal molybdates obtained by adding the salt solution of the desired metal to a solution of sodium or potassium molybdate, and (2) neutralizing a slurry or solution of molybdenum trioxide with the hydroxide or carbonate of the desired metal. For example, sodium molybdate, Na₂MoO₄, may be obtained as a dihydrate by evaporating an aqueous solution of molybdenum trioxide and sodium hydroxide. Heating the dihydrate at 100°C converts it to the anhydrous salt. Also, the normal molybdates of certain metals can be prepared by fusion of molybdenum trioxide with the desired metal oxide.

While normal molybdates of alkali metals are all water-soluble, those of other metals are only slightly soluble in water. All these salts have high melting points. Physical properties of some orthomolybdates and their CAS numbers are presented below:

Formula	CAS No.	Color	Density, g/cm ³	MP °C
Li ₂ MoO ₄	[13568-40-6]	White	2.66	702
Na ₂ MoO ₄	[7631-95-0]	White	3.28	686
K ₂ MoO ₄	[13446-49-6]	White	2.34	919
Rb ₂ MoO ₄	[13718-22-4]	White	—	958
Cs ₂ MoO ₄	[13597-64-3]	White	—	936
Ca MoO ₄	[7789-82-4]	White	4.28	985 (dec)
Sr MoO ₄	[13470-04-7]	White	4.66	1,040 (dec)
BaMoO ₄	[7787-37-3]	White	4.97	1,480
CuMoO ₄	[13767-34-5]	Light green	—	820 (dec)
Ag ₂ MoO ₄	[13765-74-7]	White	—	483
ZnMoO ₄	[13767-32-3]	White	—	700
CdMoO ₄	[13972-68-4]	Light yellow	5.35	900 (dec)
Tl ₂ MoO ₄	[34128-09-1]	White	—	Red heat
PbMoO ₄	[10190-55-3]	White	6.81	1,065
MnMoO ₄	[14013-15-1]	Yellow	—	—
FeMoO ₄	[13718-70-2]	Dark brown	—	850

CoMoO ₄	[13762-14-6]	Violet lilac	3.6	1,040
NiMoO ₄	[12673-58-4]	Green	—	970

Among molybdate salts, sodium and ammonium molybdates have commercial applications. The normal salt, sodium orthomolybdate, Na₂ MoO₄, is used in pigments. It also is used as a corrosion inhibitor and as an additive to soil. Lead molybdate, Pb MoO₄, occurs in nature as mineral ulfenite, from which molybdenum metal is recovered.

AMMONIUM MOLYBDATES

Ammonium ion forms several isopolymolybdates, including ammonium di-, tri-, hepta-, and octamolybdates. Among these, ammonium dimolybdate, (NH₄)₂Mo₂O₇ [27546-07-2] and ammonium heptamolybdate, (NH₄)Mo₇O₂₄·24H₂O [12027-67-7], and a tetrahydrate of the latter compound, (NH₄)₆Mo₇O₂₄·4H₂O [12054-85-2], have commercial applications. Ammonium heptamolybdate is used as a source of high purity molybdenum metal. All three salts are used for making specialty molybdenum catalysts. Ammonium heptamolybdate is a compound of analytical interest. When added to a solution of orthophosphate in nitric acid, it forms a yellow precipitate of ammonium phosphomolybdate, (NH₄)₃PO₄·12MoO₃. This reaction is used for colorimetric measurement of phosphate ion in water.

MOLYBDENUM BLUE

[1313-29-7]

Molybdenum blue is a mixture of several hydrous molybdenum oxides that have variable and nonstoichiometric compositions in the range Mo^VO_{2.5} to Mo^{VI}O₃. These compounds are blue solids when isolated. All compounds impart deep blue coloration to the solution. The solids are mostly amorphous and colloidal in nature; that is, they disperse in water as colloidal particles. They are sensitive to oxidation-reduction. There are several molybdenum blue compounds in crystalline state. They may be prepared either as intermediate molybdenum oxides or as their hydrates. Some examples of molybdenum blue compounds are Mo₈O₂₃; Mo₈O₂₃·8H₂O; Mo₉O₂₆; Mo₂O₅·H₂O; Mo₄O₁₁·H₂O; Mo₄O₁₀(OH)₂; Mo₂O₄(OH)₂; Mo₃O₈OH.

Molybdenum blue in amorphous form may be made by the reduction of molybdenum trioxide, MoO₃, or molybdate ion, MoO₄²⁻ in sulfuric acid solution with a reducing agent, such as, zinc, hydrazine, sulfur dioxide, hydriodic acid, hydrogen sulfide, or molybdenum metal. The solution turns intense blue and contains colloidal particles. The nature of the product greatly depends on the reducing agent, concentration of H₂SO₄, pH of the medium, and other factors. Metallic tin, copper, or zinc, or the ions Cu⁺ or Sn²⁺ effectively reduce MoO₃ only at acid strength between 25% to 75%. The blue color may disappear upon dilution of the solution or on heating (and will reappear on cooling). In neutral solution, Sn²⁺ reduces molybdic acid to form a stable blue product, the

color of which does not disappear either on heating or diluting the solution. Several other reducing agents have been used to produce molybdenum blue. They include hydroquinone in sunlight; glucose; atomic hydrogen; and lithium aluminum hydride. Action of atomic hydrogen on MoO_3 yields $\text{Mo}_2\text{O}_4(\text{OH})_2$ and $\text{Mo}_4\text{O}_{10}(\text{OH})_2$ in crystalline state. Reaction between MoO_3 and LiAlH_4 forms a crystalline compound, $\text{Mo}_5\text{O}_7(\text{OH})_8$. Electrolytic reduction of ammonium heptamolybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ in sulfuric acid solution may form $\text{Mo}_3\text{O}_8\text{OH}$, which is readily soluble in water.

Under acid conditions, molybdate reacts with orthophosphate, PO_4^{3-} to form a blue heteropoly acid, molybdophosphoric acid. A similar reaction occurs with arsenate ion, AsO_4^{3-} . In the presence of vanadium, the product is yellow vanadomolybdophosphoric acid. These reactions are used for colorimetric analyses of phosphate, arsenate, and many other substances. Colloidal molybdenum blue has limited applications such as dyeing silk. It readily absorbs onto surface-active materials.

MOLYBDENUM DISULFIDE

[1317-33-5]

Formula: MoS_2 ; MW 160.07

Synonyms: molybdenite; molybdic sulfide; molybdenum sulfide; molybdenum(IV) sulfide.

Occurrence and Uses

Molybdenum disulfide occurs in nature as mineral molybdenite. It is the principal ore from which molybdenum metal is recovered commercially. The compound is used as a dry lubricant and as an additive to lubricant. It also is used as a catalyst.

Physical Properties

Black powder or hexagonal crystal; density 5.06 g/cm^3 ; hardness 1.3 Moh's; melts at $2,375^\circ\text{C}$; insoluble in water and dilute acids; soluble in strong oxidizing acids, such as, aqua regia and boiling sulfuric acid.

Thermochemical Properties

ΔH_f°	-56.19 kcal/mol
ΔG_f°	-53.99 kcal/mol
S°	$14.96 \text{ cal/degree mol}$
C_p	$15.20 \text{ cal/degree mol}$

Production

Molybdenum disulfide is mined from natural molybdenite deposits. The compound also can be made by direct combination of elements; i.e., heating molybdenum and sulfur at elevated temperatures and under vacuum. Under such conditions, other sulfides of molybdenum that may have formed convert to the more stable disulfide.

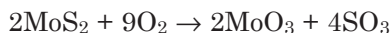
Molybdenum disulfide also may be prepared by treating molybdenum pentachloride with a solution of sodium sulfide:



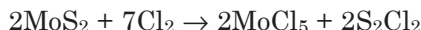
Also, the disulfide is obtained by heating molybdenum trioxide with hydrogen sulfide or sulfur.

Reactions

Molybdenum disulfide is stable in air or oxygen at ordinary temperatures but reacts with oxygen at elevated temperatures forming molybdenum trioxide:



Chlorine attacks the disulfide at elevated temperatures forming molybdenum pentachloride:



Molybdenum disulfide reacts with alkyl lithium under controlled conditions to form compounds of compositions Li_xMoS_2 (intercalation compounds). With butyl lithium, $\text{C}_4\text{H}_9\text{Li}$, the product is LiMoS_2 .

Analysis

Elemental composition: Mo 59.94%, S 40.06%. The compound or mineral molybdenite may be identified nondestructively by x-ray and from physical properties. Molybdenum content of the material may be determined by various instrumental techniques after digestion of the solid in concentrated HNO_3 or aqua regia followed by appropriate dilution of acid extract (See Molybdenum.)

MOLYBDENUM HEXACARBONYL

[13939-06-5]

Formula: $\text{Mo}(\text{CO})_6$; MW 264.00

Synonym: molybdenum carbonyl

Uses

Molybdenum hexacarbonyl is used for molybdenum plating; for deposition of metallic molybdenum in making molybdenum mirrors; and as a catalyst. It also is used to synthesize many organomolybdenum compounds.

Physical Properties

White, shiny crystals; orthogonal crystal structure; density 1.96 g/cm³; sublimes at 150°C with decomposition; vapor pressure 0.1 torr at 20°C; insoluble in water; soluble in benzene and paraffin oil; slightly soluble in ether.

Thermochemical Properties

ΔH_f° (cry)	-234.9 kcal/mol
ΔH_f° (gas)	-218.0 kcal/mol
ΔG_f° (cry)	-209.8 kcal/mol
ΔG_f° (gas)	-204.6 kcal/mol
S° (cry)	77.9 cal/degree mol
S° (gas)	117.1 cal/degree mol
C_p (cry)	57.9 cal/degree mol
C_p (gas)	49.0 cal/degree mol
ΔH_{vap}	17.3 kcal/mol

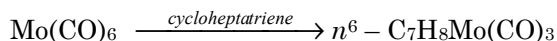
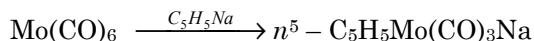
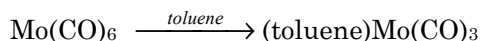
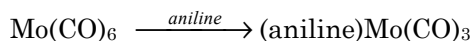
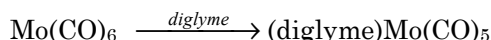
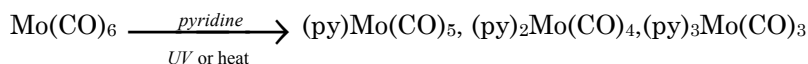
Preparation

Molybdenum hexacarbonyl usually is made by treating molybdenum pentachloride with zinc dust in carbon monoxide under high pressure (90 to 120 atm). Also, it can be prepared by direct combination of molybdenum metal powder with carbon monoxide under pressure.

Reactions

Thermal dissociation of molybdenum hexacarbonyl yields molybdenum metal and carbon monoxide.

The carbonyl undergoes a variety of complex formation reactions, involving partial or total replacement of CO groups with other donors. Many reactions have synthetic applications. Such donors include pyridine (py), diglyme, toluene, aniline, cycloheptatriene, alkyl disulfide and metal cyclopentadiene. A few examples are given below:



Molybdenum hexacarbonyl also forms carbonylate anions, Mo(CO)_5^{2-} , carbonyl halide anions, $\text{Mo(CO)}_5^{\text{x-}}$ and carbonyl hydride anions, $\text{Mo(CO)}_5\text{H}^-$ in solution under controlled conditions. These species are unstable and have not been isolated.

Reaction with a carboxylic acid, RCOOH , forms the corresponding carboxylate complex $[\text{Mo(OCOR)}_2]_2$.

Reaction with mild reducing agents, such as sodium borohydride, NaBH_4 ,

yields dimolybdenum decacarbonylate anion $[\text{Mo}_2(\text{CO})_{10}]^{2-}$ in solution.

Analysis

Elemental composition: Mo 36.34%, C 27.30%, O 36.36%. A benzene solution of the hexacarbonyl may be analyzed by GC/MS. Molybdenum metal digested in nitric acid solution may be analyzed by various instrumental techniques. Also, the compound may be thermally dissociated and the liberated CO may be identified by GC using a TCD or by GC/MS using an appropriate capillary column.

Toxicity

Molybdenum hexacarbonyl is toxic by ingestion, inhalation and other routes of exposure. It decomposes, giving toxic carbon monoxide.

MOLYBDENUM HEXAFLUORIDE

[7783-77-9]

Formula: MoF_6 ; MW 209.93

Synonym: molybdenum(VI) fluoride

Uses

Molybdenum hexafluoride is used for separation of molybdenum isotopes.

Physical Properties

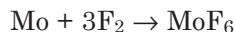
White cubic crystals or colorless volatile liquid; hygroscopic; density 2.54 g/cm^3 ; melts at 17.5°C ; boils at 34°C ; critical temperature 200°C ; critical pressure 46.88 atm ; critical volume $226 \text{ cm}^3/\text{mol}$; reacts with water (hydrolyzed).

Thermochemical Properties

$\Delta H_f^\circ (\text{l})$	-378.9 kcal/mol
$\Delta H_f^\circ (\text{g})$	-372.3 kcal/mol
$\Delta G_f^\circ (\text{l})$	-352.1 kcal/mol
$\Delta G_f^\circ (\text{g})$	-351.9 kcal/mol
$S^\circ (\text{l})$	$62.1 \text{ cal/degree mol}$
$S^\circ (\text{g})$	$83.8 \text{ cal/degree mol}$
$C_p (\text{l})$	$40.6 \text{ cal/degree mol}$
$C_p (\text{g})$	$28.7 \text{ cal/degree mol}$
ΔH_{fus}	1.03 kcal/mol
ΔH_{vap}	6.50 kcal/mol

Preparation

Molybdenum hexafluoride is prepared by passing fluorine over molybdenum powder:



Analysis

Elemental composition: Mo 45.70%, F 54.30%. The compound may be identified from its physical properties. Molybdenum may be analyzed by AA or ICP in an acid extract of the compound following digestion with nitric acid.

Toxicity

The compound is toxic by ingestion and is an irritant to skin.

MOLYBDENUM ORANGE

[12656-85-8]

Synonyms: molybdate orange; molybdate chrome orange; moly orange; molybdate red; chrome vermilion

Molybdenum orange is a solid solution of lead molybdate, lead chromate and often lead sulfate. It is used as a pigment in paints, plastics and printing inks. The pigment is used for red hues in automobile and appliance paints.

Molybdenum orange is precipitated by adding solutions of sodium chromate, sodium molybdate, and sodium sulfate to a solution of lead nitrate. The solid mixture is filtered and the precipitate is slowly dried under controlled conditions. Molybdenum orange is obtained as a fine powder of dark orange or light red color.

The compound is toxic by inhalation. There is sufficient evidence of its carcinogenicity in humans.

MOLYBDENUM(IV) OXIDE

[18868-43-4]

Formula: MoO₂; MW 127.94

Synonym: molybdenum dioxide

Physical Properties

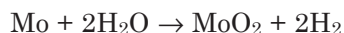
Greyish tetragonal or monoclinic crystals; density 6.47 g/cm³; insoluble in water; slightly soluble in hot concentrated sulfuric acid; insoluble in alkalies, hydrochloric acid and hydrofluoric acid.

Thermochemical Properties

ΔH_f°	-140.75 kcal/mol
ΔG_f°	-127.39 kcal/mol
S°	11.07 cal/degree mol
C_p	13.38 cal/degree mol

Preparation

Molybdenum(IV) oxide is obtained by passing steam over red hot molybdenum:



Alternatively, the oxide may be prepared by heating a molybdate salt, such as ammonium molybdate, with a reducing agent such as zinc. The dioxide also may be obtained along with other oxides of molybdenum when molybdenum metal is heated in air.

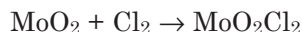
A brown-black suspension of MoO_2 in hydrate form may be obtained by reducing a solution of ammonium molybdate with hydrogen in the presence of colloidal palladium.

Reactions

The dioxide readily oxidizes to trioxide when heated in air. It also is oxidized to MoO_3 by nitric acid. When heated with hydrogen above 470°C , the oxide is reduced to molybdenum metal.

Unlike the trioxide, molybdenum dioxide is stable towards nonoxidizing acids, alkalies or fused salts.

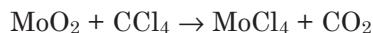
Molybdenum(IV) oxide combines with chlorine at 300°C to form dioxydichloride, MoO_2Cl_2 :



When heated above 1775°C in the absence of air, the dioxide dissociates to trioxide and metallic molybdenum:



When heated with carbon tetrachloride at elevated temperatures, the dioxide converts to molybdenum tetrachloride, MoCl_4 :



Reactions with chlorinated hydrocarbons at elevated temperatures also yield the tetrachloride.

Analysis

Elemental composition: Mo 74.99%, O 25.01%. Molybdenum oxide is identified by x-ray crystallography. Molybdenum content in the oxide can be determined by AA, ICP, or x-ray fluorescence analysis.

MOLYBDENUM(VI) OXIDE

[1313-27-5]

Formula: MoO_3 ; MW 143.94

Synonyms: molybdenum trioxide; molybdic acid anhydride; molybdic anhydride; molybdic oxide

Uses

Molybdenum(VI) oxide is used in catalyst compositions to carry out desulfurization of petroleum feedstocks and to remove nitrogen-containing compounds from petroleum fractions. Other uses of this oxide include preparation of various molybdate salts and as reagents for chemical analyses.

Physical Properties

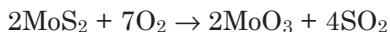
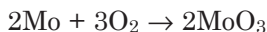
Soft white powder; orthorhombic crystals; turns yellow on heating; density 4.69 g/cm³ at 21°C; melts at 795°C without decomposition to a dark yellow liquid; vapor pressure 20 torr at 851°C and 200 torr at 1,014°C; boils at 1,155°C; sparingly soluble in cold water (1.066 g/L at 18°C) and moderately soluble in hot water (20.55 g/L at 70°C); dissolves in acids and alkalies.

Thermochemical Properties

ΔH_f°	-178.08 kcal/mol
ΔG_f°	-159.66 kcal/mol
S°	18.58 cal/degree mol
C_p	17.92 cal/degree mol

Preparation

Molybdenum(VI) oxide is obtained by igniting molybdenum or its compounds in air:

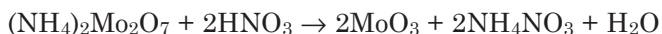


Roasting the sulfide is carried out in a multiple-hearth roaster under controlled temperature and airflow. The product mixture is sublimed to obtain high purity oxide.

Purified molybdenum(VI) oxide also is made by prolonged heating of ammonium molybdate in air:

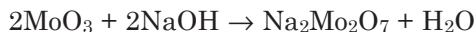


An alternative method involves repeatedly evaporating a mixture of ammonium molybdate and nitric acid. Ammonium nitrate so formed is separated from the product molybdenum(VI) oxide by extraction with water:



Reactions

Molybdenum(VI) oxide is the most stable oxide of molybdenum. It reacts with alkali solutions, forming molybdates:



Similarly, ammonium dimolybdate, $(\text{NH}_4)_2\text{Mo}_2\text{O}_7$, crystallizes when aqueous solutions of MoO_3 containing excess ammonia are evaporated at 100°C . Crystallization at low temperatures, however, forms ammonium heptamolybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, instead of dimolybdate.

Molybdenum(VI) oxide combines with several metal oxides forming their orthomolybdates. Such products are obtained as hydrated salts upon neutralization of slurries of MoO_3 and the metal oxides with alkalis:



When heated with sulfur vapor, molybdenum disulfide, MoS_2 , is obtained.

Reaction with alkali fluorides (except LiF) yields double salts, such as $\text{K}_3[\text{MoO}_3\text{F}_3]$, formed as colorless cubic crystals.

When heated in dry hydrogen chloride, MoO_3 forms a hydrochloride adduct, $\text{MoO}_3 \cdot 2\text{HCl}$, obtained as a sublimate of pale yellow needles.

A sulfuric acid solution of the oxide (25-75% solution) can be reduced with tin, copper, zinc, and other reducing agents forming a blue solution of "molybdenum blue" which are hydrous oxides of non-stoichiometric compositions (see Molybdenum Blue). Reduction with atomic hydrogen under carefully controlled conditions yields colloidal dispersion of compounds that have probable compositions $\text{Mo}_2\text{O}_4(\text{OH})_2$ and $\text{Mo}_4\text{O}_{10}(\text{OH})_2$. Reduction with lithium aluminum hydride yields a red compound of probable composition $\text{Mo}_5\text{O}_7(\text{OH})_8$. Molybdenum(VI) oxide suspension in water also can be reduced to molybdenum blue by hydriodic acid, hydrazine, sulfur dioxide, and other reductants.

Molybdenum(VI) oxide behaves as a basic oxide in reactions with strong acids. Thus it forms an oxychloride, $\text{MoO}(\text{OH})_2\text{Cl}_2$, with hydrochloric acid. Sulfuric acid forms an oxysulfate, MoO_2SO_4 .

Heating with chlorine at 500°C yields MoO_2Cl_2 and with bromine vapor the products are MoO_2Br_2 and $\text{Mo}_2\text{O}_3\text{Br}_4$.

When heated with finely divided molybdenum at 750°C , molybdenum trioxide converts to pentaoxide, Mo_2O_5 .

Analysis

Elemental composition: Mo 66.66%, O 33.34%. Molybdenum(VI) oxide may be identified from its physical and chemical properties and by x-ray analysis. Molybdenum content in the oxide can be measured by various instrumental techniques (see Molybdenum).

Toxicity

Molybdenum trioxide has been found to be toxic in experimental animals by oral, dermal, and intraperitoneal routes.

LD₅₀ oral (rat): 125mg/kg

LD₅₀ subcutaneous (mouse): 94 mg/kg

MOLYBDENUM PENTACHLORIDE

[10241-05-1]

Formula: MoCl₅; MW 273.20; monomeric in vapor phase but occurs as dimeric Mo₂Cl₁₀ in solid phase (Mo—Mo bond 3.84 Å)

Synonym: molybdenum(V) chloride

Uses

Molybdenum pentachloride is used as a catalyst in chlorination reactions. It also is used in fire-retardant resins; for soldering of flux; for deposition of molybdenum coating; and to prepare several other molybdenum compounds, including molybdenum oxychlorides and hexacarbonyl.

Physical Properties

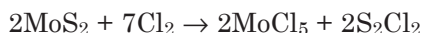
Greenish-black monoclinic crystals or dark red as liquid or vapor; paramagnetic; hygroscopic; density 2.93 g/cm³; melts at 194°C; boils at 268°C; vapor density 9.5 (air=1) at 350°C; critical temperature 577°C; critical volume 369 cm³/mol; soluble in dry ether, dry alcohol and many other organic solvents; reacts with water.

Thermochemical Properties

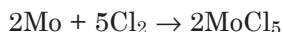
ΔH_{vap}	15.0 kcal/mol
ΔH_{fus}	4.54 kcal/mol

Preparation

Molybdenum pentachloride may be prepared by heating molybdenite in chlorine. Sulfur chloride formed in the reaction is removed by distillation:



Also, the compound may be prepared by the action of chlorine on molybdenum metal at elevated temperatures (500°C):



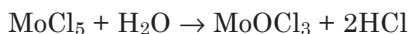
The pentachloride may be obtained from the tetrachloride, MoCl₄. The latter, when heated in a sealed tube sublimes, and upon cooling, disproportion-

ates to MoCl_5 and the trichloride, MoCl_3 :



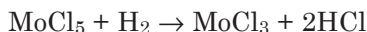
Reactions

Molybdenum pentachloride is hydrolyzed readily in water forming an oxychloride, MoOCl_3 . The reaction proceeds with hissing noise and evolution of heat.



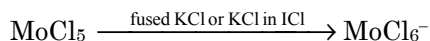
It forms the oxychlorides MoOCl_3 and MoO_2Cl_2 in contact with air or oxygen. MoOCl_3 is thermodynamically the most stable oxychloride.

When heated with hydrogen at 400°C or the vapors passed over heated molybdenum metal, the pentachloride converts to trichloride:

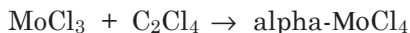


When refluxed in benzene, the pentachloride converts to tetrachloride, MoCl_4 .

Reaction with potassium chloride in fused state or in the presence of iodine monochloride forms molybdenum hexachloride anion, MoCl_6^{2-} , which forms salts such as K_2MoCl_6 :



Reaction with tetrachloroethylene forms molybdenum tetrachloride (an alpha-isomer of MoCl_4 that is isomorphous with NbCl_4 .)



However, when the pentachloride is heated with hydrocarbons, a beta-form of MoCl_4 forms. The product always is contaminated with carbon. Heating the pentachloride with molybdenum metal forms the same beta- MoCl_4 . Reaction with hydrogen bromide yields molybdenum tetrabromide.

Molybdenum pentachloride forms mixed complexes and oxychloride adducts with several donors. Thus, the adducts with pyridine, bipyridyl and alkyl nitriles are $\text{MoCl}_4(\text{py})_2$, $\text{MoCl}_4(\text{bipy})$ and $\text{MoCl}_4(\text{RCN})_2$, respectively.

Combination with bipyridyl ligand in carbon tetrachloride followed by hydrolysis yields a molybdenum oxychloride bipyridyl complex of formula $\text{MoOCl}_3(\text{bipy})$. When mixed with ammonium chloride in acetonitrile and water, an oxychloride-acetonitrile complex, $\text{NH}_4[\text{MoOCl}_4\text{CH}_3\text{CN}]$, is obtained.

Reactions with triphenylphosphine oxide, $(\text{C}_6\text{H}_5)_3\text{P}=\text{O}$, forms two products, an orange complex $\text{MoO}_2\text{Cl}_2[\text{O}(\text{C}_6\text{H}_5)_3]_2$ and a green complex, $\text{MoOCl}_3[\text{O}(\text{C}_6\text{H}_5)_3]_2$ (Cotton, F. A., Wilkinson, G., Murillo, C. A. and M. Bochmann. 1999. *Advanced Inorganic Chemistry*, 6th ed. p. 936: New York: John Wiley & Sons).

Analysis

Elemental composition: Mo 35.12%, Cl 64.88%. Molybdenum pentachloride may be identified from its physical properties and the products it forms in various reactions. The molybdenum content may be measured by flame or furnace-AA or ICP/AES measurement following digestion with nitric acid and appropriate dilution.

Toxicity

The compound is toxic by all routes of exposure and is corrosive to skin and eyes. The vapors irritate mucous membranes.

NEODYMIUM

[7440-00-8]

Symbol Nd; atomic number 60; atomic weight 144.24; a rare earth lanthanide element; a light rare earth metal of cerium group; an inner transition metal characterized by partially filled 4f subshell; electron configuration [Xe]4f³5d¹6s²; most common valence state +3; other oxidation state +2; standard electrode potential, $\text{Nd}^{3+} + 3\text{e}^- \leftrightarrow -2.323 \text{ V}$; atomic radius 1.821 Å (for CN 12); ionic radius, Nd^{3+} 0.995 Å; atomic volume 20.60 cc/mol; ionization potential 6.31 eV; seven stable isotopes: Nd-142 (27.13%), Nd-143 (12.20%), Nd-144 (23.87%), Nd-145 (8.29%), Nd-146 (17.18%), Nd-148 (5.72%), Nd-150 (5.60%); twenty-three radioisotopes are known in the mass range 127-141, 147, 149, 151-156.

History, Occurrence, and Uses

The element was discovered by von Welsbach in 1885 after he succeeded in fractionating ammonium didymium nitrate, thus splitting didymia into two new rare earths. Earlier, in 1841, Mosander extracted a rose-colored oxide from cerite, which he named didymium and which actually was a mixture of two rare earth elements. These two new elements were named by von Welsbach as *praseodymia* (green twin) and *neodymia* (new twin).

Neodymium occurs in nature in the minerals bastnasite, monazite, cerite and allanite. The element always is associated with other rare earths, especially cerium group elements. Its abundance in the earth's crust is about 0.0024%.

The pure metal has very little commercial application. However, in the form of alloys neodymium has found some important but limited applications in metallurgy. It is added to cast iron, magnesium, aluminum, zirconium and titanium alloys. It imparts high temperature strength and creep resistance to these alloys. It acts as a "getter" for oxygen, sulfur, hydrogen, nitrogen and other elements. Small quantities of neodymium salts are used as a coloring agent for glass and porcelain, imparting red color. Neodymium oxide, Nd_2O_3 , incorporated into glass is used as a laser material to produce coherent light. Its mixture with praseodymium, commonly known as didymium [8006-73-3] is used in making glass-blowing and welding goggles to protect eyes from

sodium light. Such glass also is used in astronomy to produce sharp bands and calibrate spectral lines.

Physical Properties

Silvery-white, soft malleable metal; exists in two allotropic forms: an alpha hexagonal form and a beta form that has body-centered cubic crystal structure; the alpha allotrope converts to beta modification at 868°C; paramagnetic; density 7.004 g/cm³; compressibility 3.0x10⁻⁶ cm³/kg; melts at 1024°C; vaporizes at 3027°C; vapor pressure 400 torr at 2870°C; electrical resistivity 65x10⁻⁶ ohm-cm (as measured on polycrystalline wire at 25°C); Young's modulus 3.79x10⁻¹¹ dynes/cm²; Poisson's ratio 0.306; thermal neutron cross section 46 barns.

Thermochemical Properties

ΔH_f° (cry)	0.0
ΔH_f° (gas)	78.3 kcal/mol
ΔG_f° (cry)	0.0
ΔG_f° (gas)	69.9 kcal/mol
S° (cry)	17.1 cal/degree mol
S° (gas)	45.2 cal/degree mol
C_p (cry)	6.56 cal/degree mol
C_p (gas)	5.28 cal/degree mol
ΔH_{fus}	1.70 kcal/mol
ΔH_{vap}	78.5 kcal/mol
Thermal conductivity (at 28°C)	0.031 cal/cm ² /sec/°C

Reactions

Neodymium corrodes slowly in dry atmosphere at ambient temperature. However, in moist air, the rate of oxidation is faster, forming a hydrated oxide. At elevated temperatures, the metal combines with oxygen, forming neodymium sesquioxide. Above 200°C the metal burns in halogens forming halides. Neodymium combines with many nonmetallic elements including hydrogen, nitrogen, carbon, phosphorus, and sulfur at elevated temperatures forming their binary compounds. With hydrogen, products are interstitial hydrides, NdH₂ and NdH₃. It combines with metalloid elements boron, selenium, and arsenic at elevated temperatures forming the corresponding boride, selenide, and arsenide respectively.

The metal dissolves in dilute mineral acids, but concentrated sulfuric acid has little action on it. Its surface passivates when immersed in 2 to 5% solution of nitric acid in ethanol. A protective oxide layer forms over the metal surface, which prevents any further contact.

Neodymium is a moderately strong reducing agent. It reduces several metal oxides, such as magnesia, alumina, silica, and zirconia at elevated temperatures, converting these oxides to their metals.

Production

Neodymium is recovered mostly from mineral monazite and bastnasite, the

two most abundant rare-earth minerals. Monazite is a rare earth-thorium phosphate usually containing between 9 to 20% neodymium. Bastnasite is a rare earth fluocarbonate ore containing 2 to 15% neodymium. Both ores are first cracked by heating with concentrated sulfuric acid or sodium hydroxide. The recovery process from monazite ore using sulfuric acid is described below:

Heating the ore with sulfuric acid converts neodymium to its water soluble sulfate. The product mixture is treated with excess water to separate neodymium as soluble sulfate from the water-insoluble sulfates of other metals, as well as from other residues. If monazite is the starting material, thorium is separated from neodymium and other soluble rare earth sulfates by treating the solution with sodium pyrophosphate. This precipitates thorium pyrophosphate. Alternatively, thorium may be selectively precipitated as thorium hydroxide by partially neutralizing the solution with caustic soda at pH 3 to 4. The solution then is treated with ammonium oxalate to precipitate rare earth metals as their insoluble oxalates. The rare earth oxalates obtained are decomposed to oxides by calcining in the presence of air. Composition of individual oxides in such rare earth oxide mixture may vary with the source of ore and may contain neodymium oxide, as much as 18%.

The oxalates obtained above, alternatively, are digested with sodium hydroxide converting the rare earth metals to hydroxides. Cerium forms a tetravalent hydroxide, $\text{Ce}(\text{OH})_4$, which is insoluble in dilute nitric acid. When dilute nitric acid is added to this rare earth hydroxide mixture, cerium(IV) hydroxide forms an insoluble basic nitrate, which is filtered out from the solution. Cerium also may be removed by several other procedures. One such method involves calcining rare earth hydroxides at 500°C in air. Cerium converts to tetravalent oxide, CeO_2 , while other lanthanides are oxidized to trivalent oxides. The oxides are dissolved in moderately concentrated nitric acid. Ceric nitrate so formed and any remaining thorium nitrate present is now removed from the nitrate solution by contact with tributyl phosphate in a countercurrent.

After removing cerium (and thorium), the nitric acid solution of rare earths is treated with ammonium nitrate. Lanthanum forms the least soluble double salt with ammonium nitrate, which may be removed from the solution by repeated crystallization. Neodymium is recovered from this solution as the double magnesium nitrate by continued fractionation.

Three alternative methods may be mentioned here, which give high purity material and are less tedious than the one described above. These are (1) ion exchange, (2) metallothermic reduction, and (3) electrolysis.

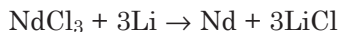
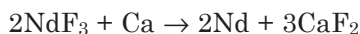
In the ion exchange process, the nitric acid solution of the rare earth oxides obtained above is passed through a sulfonated styrene-divinylbenzene copolymer or other cation exchange resin in the hydrogen form. The rare earths are selectively eluted by flowing down a chelating solution of ethylenediamine tetraacetic acid (EDTA), or citric acid, or nitrilotriacetate (NTA) through the loaded column. The most stable complexes are eluted first. Metal ions are selectively stripped out in successive stages.

In the metallothermal reduction, the mixture of rare earth oxides obtained above is first converted to their halide salts. This is done by heating the oxides

at 300 to 400°C with dry and purified hydrogen fluoride, or preferably, by allowing dry hydrogen fluoride to pass over rare earth oxides and ammonium fluoride at 300-400°C. If chloride salt is desired, the oxides must be heated with ammonium chloride. For example, neodymium oxide may be converted to its fluoride or chloride:



Neodymium, along with lanthanum, cerium and praseodymium, has low melting points and high boiling points. The fluorides of these and other rare earth metals are placed under highly purified helium or argon atmosphere in a platinum, tantalum or tungsten crucible in a furnace. They are heated under this inert atmosphere or under vacuum at 1000 to 1500°C with an alkali or alkaline earth metal. The halides are reduced to their metals:



The crucible is allowed to cool and is held at a temperature slightly above the melting point of neodymium for a sufficient time to allow separation of the metal.

In the electrolytic process, a fused mixture of anhydrous rare earth chlorides (obtained above) and sodium or potassium chloride is electrolyzed in an electrolytic cell at 800 to 900°C using graphite rods as the anode. The cell is constructed of iron, carbon or refractory linings. Molten metal settles to the bottom and is removed periodically.

Analysis

Neodymium may be analyzed by x-ray diffraction, x-ray fluorescence, atomic absorption, or atomic emission spectrometry. Also, the metal may be identified and measured by neutron activation analysis.

NEODYMIUM OXIDE

[1313-97-9]

Formula: Nd_2O_3 ; MW 336.48

Synonyms: neodymia; neodymium sesquioxide

Uses

Neodymium oxide is incorporated into glass to impart a bright purple color. It also is used in protective filter lenses for welding and glass-blowing goggles; and for polishing glasses. The compound is applied as a doping material for

yttrium aluminum microwave devices; and to activate calcium tungstate, calcium silicate, and other host crystals for their applications in room temperature lasers. The oxide also is used as a catalyst for dehydrogenation of alcohol.

Physical Properties

Blue powder; hexagonal crystals; fluoresces red; density 7.24 g/cm³; melts around 1,900°C; practically insoluble in water, 30 mg/L at 75°C; dissolves in acids.

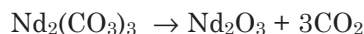
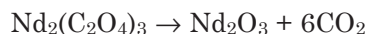
Thermochemical Properties

ΔH_f°	-432.1 kcal/mol
ΔG_f°	-411.3 kcal/mol
S°	37.9 cal/degree mol
C_p	26.6 cal/degree mol

Production

Neodymium oxide is produced from the two principal rare earth minerals, monazite, and bastnasite. The oxide is obtained as an intermediate in the recovery of neodymium metal (See Neodymium).

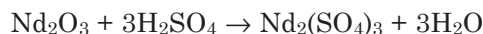
The oxide also may be formed by thermal dissociation of neodymium oxalate, hydroxide or carbonate:



Reactions

The anhydrous oxide absorbs moisture from the air at ambient temperatures forming hydrated oxide. The oxide also absorbs carbon dioxide from air, forming neodymium carbonate.

Neodymium oxide dissolves in strong mineral acids forming corresponding neodymium salts:

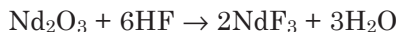


Reactions with acetic and other organic acids produce corresponding salts.

When heated with ammonium chloride at 300 to 400°C, the oxide converts to chloride liberating ammonia and water:



When heated with hydrogen fluoride, the product is neodymium fluoride:



The oxide is reduced to neodymium metal when heated with hydrogen, carbon monoxide, or other reducing agents.

Analysis

Elemental composition: Nd 85.73%, O 14.27%. The oxide may be characterized by x-ray diffraction and fluorescent properties. Neodymium may be analyzed in an acid extract of the oxide by ICP-AES or ICP-MS techniques under appropriate dilution of the extract.

NEON

[7440-01-9]

Symbol Ne; atomic number 10; atomic weight 20.179; an inert gas; a Group VIII or Group 0 (Group 18) noble gas element; electron configuration $1s^2 2s^2 2p^6$; valence 0; atomic radius 0.71Å; three stable isotopes, Ne-20 (90.48%), Ne-21 (0.27%), Ne-22 (9.25%); ten short-lived artificial isotopes are known in the mass range 17-19, 23-29; half-life of longest radioactive isotope Ne-24 is 3.34 min.

History, Occurrence, and Uses

Neon was discovered by Ramsay and Travers in 1898. Its name comes from the Greek word *neos*, which means new. It is present in the atmosphere at a concentration of 0.00182% by volume (dry atmosphere). This element also is found in stars and interstellar gas clouds. Earth's earliest crust probably contained neon occluded in minerals. The gas later escaped into the atmosphere.

The most important use of this gas is in the 'neon' lights and fluorescent signs for advertisements. Neon contained in glow discharge lamps or high voltage discharge tubes at low pressure emits red light. In the presence of mercury vapors, the color of the glow turns blue. Neon also is used in sodium vapor lamps for street lighting and in various pilot lamps for electronic equipments. In most types of fluorescent lights neon is used in combination with other inert gases, usually argon, krypton, and xenon.

Neon is also used in scintillation counters, neutron fission counters, proportional counters, and ionization chambers for detection of charged particles. Its mixtures with bromine vapors or chlorine are used in Geiger tubes for counting nuclear particles. Helium-neon mixture is used in gas lasers. Some other applications of neon are in antifog devices, electrical current detectors, and lightning arrestors. The gas is also used in welding and preparative reactions. In preparative reactions it provides an inert atmosphere to shield the reaction from air contact.

Physical Properties

Colorless, odorless, tasteless gas; gas density 0.9002 g/L at 0°C; liquid density 1.206 g/mL at its boiling point; liquefies at -245.9°C; solidifies at -248.67°C; forming face-centered cubic crystals; critical temperature -228.75°C; critical pressure 26.9 atm; solubility in water at 20°C, 10.5 mL/L.

Production

Neon is derived commercially from the atmosphere. It is recovered from air after separation of oxygen and nitrogen in air separation plants. The recovery process is based on liquefaction of air. Neon and helium have boiling points below that of liquid air. Thus, at liquid air temperature, nitrogen, oxygen, argon, krypton, and xenon remain in the liquid form, while a gas stream consisting of neon, helium, and some nitrogen is collected as gaseous mixture. The composition of this mixture can vary with the condenser and rate of withdrawal. Nitrogen is removed further by passing the gaseous mixture at 5 to 6 atm through a condenser maintained at liquid nitrogen temperatures. The residue after this step contains neon as the major component, with significant amounts of helium, hydrogen, and nitrogen.

Such crude neon mixture is purified by various chemical and physical processes. Hydrogen is separated by chemically oxidizing it to water, which is removed by drying. Remaining nitrogen from the crude neon is removed by adsorption over charcoal at the liquid nitrogen temperature. After the removal of nitrogen and hydrogen, the technical grade neon may contain about 75% neon and 25% helium. Such neon-helium mixtures may be further separated into their individual components either by differential absorption on charcoal at cold temperatures or by fractional distillation of their liquefied mixture. Fractional distillation, based on the difference of boiling points between helium (-269°C) and neon (-223°C), is the more expensive process. Neon also may be obtained in liquid form if the charcoal in the adsorption process is maintained at its liquefaction temperature. Process conditions may vary depending on purity of the product desired.

Compounds

Being a zero valent element and having a highly stable octet configuration, neon is inert to practically all chemicals. However, unlike some other inert gases such as xenon which forms fluorides, oxides, or oxofluorides or argon, which forms clathrates, no such compounds are known for neon. Neon forms an unstable hydrate at low temperature under high pressure. It does ionize, however, under high vacuum as in the electric discharge tube, forming ions such as Ne_2^+ , $(\text{HeNe})^+$, NeH^+ , and $(\text{NeAr})^+$. Such ions have been identified from optical and mass spectroscopic studies.

Analysis

Neon may be analyzed by GC using a thermal conductivity or a flame ionization detector. The gas may be measured by GC/MS using a capillary column. Characteristic masses for its GC/MS identification are 20 and 22.

NEPTUNIUM

[7439-99-8]

Symbol Np; atomic number 93; atomic weight 237 (most stable isotope); a man-made transuranium radioactive element; actinide series; electron configuration $[\text{Rn}]5f^46d^17s^2$; oxidation states +3, +4, +5 and +6; most stable valence

state +3; the longest-lived isotope Np-237 has a half-life of 2.14×10^6 year; seventeen isotopes are known in the mass range 226-242.

History, Occurrence, and Uses

Neptunium, the first transuranium element, was discovered by E. M. McMillan and P. H. Abelson in 1940 in Berkeley, California. It was produced in the cyclotron in a nuclear reaction by bombarding uranium-238 with neutrons. An isotope of mass 239 and atomic number 93 and $t_{1/2}$ of 2.4 days was produced in this reaction. Neptunium-237, the longest-lived alpha-emitter with half-life 2.14×10^6 years, was discovered two years later in 1942 by Wahl and Seaborg. The new element was named after the planet Neptune, the planet next to Uranus in the solar system.

Neptunium is not found in nature in any extractable quantities. However, it occurs in uranium ores in exceedingly small concentrations resulting from neutron capture of uranium isotopes. No major application is known for this element. Its isotope, Np-237, is used in neutron detection instruments.

Physical Properties

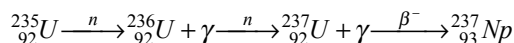
Silvery-white metal; exhibits three crystalline modifications: an orthorhombic alpha form, stable at ordinary temperatures and density 20.45 g/cm^3 ; the alpha-form transforms to a tetragonal beta allotrope of density 19.36 g/cm^3 when heated at 280°C ; the beta form converts to a body-centered cubic crystalline gamma modification at 577°C , having a density 18.0 g/cm^3 .

The metal melts at 644°C ; boils at $3,902^\circ\text{C}$ (estimated); dissolves in hydrochloric acid.

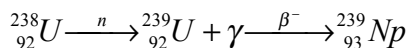
Production

Neptunium-237 is obtained as a by-product of making plutonium from uranium isotopes in nuclear reactors. Significant amounts of this element may be recovered from plutonium plant nuclear wastes. Both the recovery and purification of neptunium can be carried out by various chemical processes, including precipitation, solvent extraction and ion exchange.

Neptunium-237 may be synthesized by bombarding uranium-235 or uranium-238 with neutrons:



Neptunium-239 may be obtained from uranium-238 by neutron bombardment as it was first produced:



Neptunium may be prepared in the metallic state by the reduction of its trifluoride with barium vapor at $1,200^\circ\text{C}$ followed by rapid cooling. Its tetrafluoride may be reduced with excess calcium metal at about 750°C under argon atmosphere.

Neptunium Compounds

Neptunium is a reactive metal. Some of its chemical properties are similar to uranium and plutonium. Neptunium exists in several oxidation states, both in solutions and solid crystals. Several compounds have been well characterized by x-ray crystallography. Among its oxides, the green dioxide, NpO_2 may be obtained by thermal decomposition of its nitrate, hydroxide, or oxalate at 700 to 800°C. Two other oxides, a dark brown Np_2O_5 and a brown Np_3O_8 , also are known. All these oxides may be prepared by several methods, including heating the hydroxide $\text{Np}(\text{OH})_5$ in air above 275°C, or by treating neptunium metal with molten lithium perchlorate in the presence of ozone.

Neptunium forms a number of halides in various oxidation states. These include tri-, tetra- and hexafluorides of compositions NpF_3 , NpF_4 , and NpF_6 , respectively; trichloride, NpCl_3 and tetrachloride, NpCl_4 ; tribromide, NpBr_3 ; and the triiodide NpI_3 . Neptunium fluorides are formed by heating neptunium dioxide at elevated temperatures with fluorine in the presence of hydrogen fluoride. The tetrachloride, NpCl_4 is obtained similarly by heating the dioxide with carbon tetrachloride vapor at temperatures above 500°C. Neptunium tribromide and triiodide are prepared by heating the dioxide in a sealed vessel at 400°C with aluminum bromide and aluminum iodide, respectively.

Neptunium metal reacts with hydrogen under milder conditions at 50°C and one atmospheric pressure, forming hydrides of varying stoichiometric compositions. The metal combines with carbon at 1,200°C, forming two carbides, NpC and Np_2C_3 . Heating the trifluoride, NpF_3 with silicon at 1,500°C forms neptunium silicide, NpSi_2 . Many other neptunium compounds have been prepared and their crystal structures determined. These include the black orthorhombic sulfide, Np_2S_3 , and the tetragonal oxysulfide, NpOS , and the pink hexagonal oxofluoride, NpO_2F_2 . Neptunium also is known to form many intermetallic compounds with aluminum, beryllium and other metals.

In solution, neptunium oxidizes to Np^{3+} and Np^{4+} ions, the salts of which are pink and greenish-yellow, respectively. Unlike its rare earth analog promethium, neptunium also forms oxoions, such as, NpO^+ (blue green) and NpO^{2+} (light pink).

NICKEL

[7440-02-0]

Symbol: Ni; atomic number 28; atomic weight 58.693; a transition metal element in the first triad of Group VIII(Group 10) after iron and cobalt; electron configuration $[\text{Ar}]3d^84s^2$; valence states 0, +1, +2, and +3; most common oxidation state +2; the standard electrode potential, $\text{Ni}^{2+} + 2e^- \leftrightarrow \text{Ni}$ -0.237 V; atomic radius 1.24Å; ionic radius (Ni^{2+}) 0.70Å; five natural isotopes: Ni-58 (68.08%), Ni-60 (26.22%), Ni-61 (1.14%), Ni-62 (3.63%), Ni-64 (0.93%); nineteen radioactive isotopes are known in the mass range 51-57, 59, 63, 65-74; the longest-lived radioisotope Ni-59 has a half-life 7.6×10^4 years.

History, Occurrence, and Uses

Nickel was isolated first and recognized as an element by Cronstedt in 1751. The metal was derived in pure form by Richter in 1804. The metal takes its name from two German words 'Nickel' and 'kupfernickel', which mean Old Nick's (or Satan) and Old Nick's copper, respectively.

The abundance of nickel in the earth's crust is only 84 mg/kg, the 24th most abundant element. It is found in most meteorites, particularly in the iron meteorites or siderites, alloyed with iron. Its average concentration in seawater is 0.56 µg/mL. Nickel is one of the major components of the earth's core, comprising about 7%.

The most common nickel ores are pentlandite, $(\text{Ni,Fe})_9\text{S}_{16}$, limonite, $(\text{Fe,Ni})\text{O}(\text{OH}) \cdot n\text{H}_2\text{O}$, and garnierite, $(\text{Ni,Mg})_6\text{Si}_4\text{O}_{10}(\text{OH})_8$. Other ores that are of rare occurrence are the sulfide ores, millerite, NiS , polydymite Ni_3S_4 and siegenite, $(\text{Co,Ni})_3\text{S}_4$; the arsenide ores niccolite, NiAs , gersdorffite, NiAsS , and annabergite, $\text{Ni}_3\text{As}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$; and the antimonide ore, NiSb .

The most important applications of nickel metal involve its use in numerous alloys. Such alloys are used to construct various equipment, reaction vessels, plumbing parts, missile, and aerospace components. Such nickel-based alloys include Monel, Inconel, Hastelloy, Nichrome, Duranickel, Udinet, Incoloy and many other alloys under various other trade names. The metal itself has some major uses. Nickel anodes are used for nickel plating of many base metals to enhance their resistance to corrosion. Nickel-plated metals are used in various equipment, machine parts, printing plates, and many household items such as scissors, keys, clips, pins, and decorative pieces. Nickel powder is used as porous electrodes in storage batteries and fuel cells.

Another major industrial use of nickel is in catalysis. Nickel and raney nickel are used in catalytic hydrogenation or dehydrogenation of organic compounds including olefins, fats, and oils.

Physical Properties

Silvery-white lustrous metal; face-centered cubic crystal structure; ductile; ferromagnetic; density 8.908 g/cm³ at 20°C; hardness 3.8 Mohs; melts at 1,455°C; vaporizes at 2,730°C; electrical resistivity 6.97 microhm-cm at 20°C; total emissivity 0.045, 0.060 and 0.190 erg/s.cm² at 25, 100 and 1,000°C, respectively; modulus of elasticity (tension) 206.0x10³ MPa, modulus of elasticity (shear) 73.6x10³ MPa; Poisson's ratio 0.30; thermal neutron cross section (for neutron velocity of 2,200 m/s): absorption 4.5 barns, reaction cross section 17.5 barns; insoluble in water; dissolves in dilute nitric acid; slightly soluble in dilute HCl and H₂SO₄; insoluble in ammonia solution.

Thermochemical Properties

ΔH_f° (cry)	0.0
ΔH_f° (gas)	102.7 kcal/mol
ΔG_f° (cry)	0.0
ΔG_f° (gas)	91.9 kcal/mol
S° (cry)	7.14 cal/degree mol
S° (gas)	43.52 cal/degree mol
C_p (cry)	6.23 cal/degree mol

C_p (gas)	5.58 cal/degree mol
Co-efficient of thermal expansion	$13.3 \times 10^{-6}/^{\circ}\text{C}$ (at 0-100°C)
Thermal conductivity (at 100°C)	82.8 W/m.K

Production

Nickel usually is recovered from its sulfide ore, pentlandite $(\text{Ni,Fe})_9\text{S}_{16}$. Although laterite type oxide ores sometimes are used as starting materials, pentlandite is used in many commercial operations. Pentlandite often is found in nature associated with other sulfide minerals, such as pyrrhotite, Fe_7S_8 , and chalcopyrite, CuFeS_2 .

The ores are crushed and powdered. Sulfides are separated from gangue by froth flotation or magnetic separation processes. After this, the ore is subjected to roasting and smelting. These steps are carried out initially in rotary kilns or multihearth furnaces and then smelting is done in either blast furnaces or reverberatory, or arc furnaces. Most sulfur is removed as sulfur dioxide. Iron and other oxides produced in roasting are also removed along with siliceous slag during smelting. A matte obtained after smelting usually contains impure nickel-iron-copper sulfides and sulfur. The molten matte is treated with silica and an air blower in a converter in the Bessemerizing stage to remove all remaining iron and sulfur.

Copper-nickel matte obtained in this stage is allowed to cool slowly over a few days to separate mineral crystals of copper sulfide, nickel sulfide and nickel-copper alloy. The cool matte is pulverized to isolate sulfides of nickel and copper by froth flotation. Nickel-copper alloy is extracted by magnetic separation. Nickel metal is obtained from the nickel sulfide by electrolysis using crude nickel sulfide cast into anodes and nickel-plated stainless steel cathodes.

Alternatively, nickel sulfide is roasted to nickel oxide, which then is reduced to crude nickel and is electrorefined as above.

Two other refining processes are also frequently employed. One involves hydrometallurgical refining in which sulfide concentrates are leached with ammonia solution to convert the copper, nickel, and cobalt sulfides into their complex amines. Copper is precipitated from this solution upon heating. Under such conditions, the sulfide-amine mixture of nickel and cobalt are oxidized to their sulfates. The sulfates then are reduced to metallic nickel and cobalt by heating with hydrogen at elevated temperatures under pressure. The metals are obtained in their powder form.

The more common carbonyl refining process involves reaction of crude nickel with carbon monoxide under pressure at 100°C to form nickel tetracarbonyl, $\text{Ni}(\text{CO})_4$. The liquid tetracarbonyl upon heating at 300°C decomposes to nickel metal and carbon monoxide. Very pure nickel can be obtained by the carbonyl refining processes, as no other metal forms a similar carbonyl under these conditions.

Reactions

At ordinary temperatures, bulk nickel in compact form has no perceptible reactivity with air or water. However, in finely-divided state, the metal reacts

readily and can be pyrophoric under certain conditions. When heated in air at 400°C or with steam, nickel converts to its oxide, NiO.

When heated with bromine vapors or chlorine gas, nickel catches fire forming nickel bromide, NiBr₂, and yellow nickel chloride, NiCl₂, respectively.

Finely divided nickel combines with carbon monoxide to form zero valent nickel tetracarbonyl, Ni(CO)₄. The reaction occurs at 50°C and one atmosphere, although it is usually carried out at 200°C under high CO pressure between 100 to 400 atm for high yield of carbonyl, and to prevent product decomposition. Carbon monoxide at ordinary pressure may be passed over freshly reduced metal to form the tetracarbonyl.

Finely divided nickel absorbs a large volume of hydrogen at high temperatures. Even at ordinary temperatures, considerable occlusion of hydrogen occurs on to the metal surface and no definite composition of any hydride formed is known. The metal activates molecular hydrogen to its atomic state, contributing to its catalytic action in hydrogenation of unsaturated compounds.

Dilute mineral acids attack nickel to a varying extent. The metal dissolves readily in dilute nitric acid. Evaporation of the solution forms emerald green crystals of nickel nitrate hexahydrate, Ni(NO₃)₂ · 6H₂O.

Actions of dilute hydrochloric and sulfuric acid on nickel are relatively slow: slower than on iron. Concentrated nitric acid passivates the metal, oxidizing it and forming a protective film on its surface which prevents any further reaction.

Nickel is stable in caustic alkalies. At moderate temperatures, it decomposes gaseous ammonia into hydrogen and nitrogen. Nickel combines with sulfur, phosphorus, carbon, arsenic, antimony, and aluminum at elevated temperatures. Fusion of nickel powder with molten sulfur yields nickel sulfide, NiS. Reaction with aluminum can be explosive at 1,300°C, forming nickel-aluminum intermetallic products of varying compositions.

Nickel powder combines with carbon dioxide in ammonia solution forming nickel carbonate. Boiling the solution to expel ammonia precipitates pure carbonate, NiCO₃.

Fine nickel powder reacts with sulfamic acid in hot aqueous solution under controlled conditions, forming nickel sulfamate tetrahydrate, Ni(SO₃NH₂)₂ · 4H₂O, used in electroplating baths.

Analysis

Nickel may be measured quantitatively by several microanalytical gravimetric methods that include: (1) formation of a red precipitate with dimethylglyoxime, (2) precipitation as a black sulfide with ammonium sulfide, (3) precipitating as a complex cyanide by treating with alkali cyanide and bromine, and (4) precipitation as a yellow complex by treating an ammoniacal solution of nickel with dicyandiamide sulfate (Grossman's reagent), followed by the addition of potassium hydroxide. All of these methods can separate nickel from cobalt in solution.

Nickel, however, may be measured more accurately and rapidly at trace concentrations by various instrumental techniques including flame and fur-

nace AA, ICP/AES, ICP-MS, and x-ray fluorescence. The wavelength at which nickel is measured by AA is 232.0 nm. For flame AA measurement, air-acetylene is recommended as a flame gas. The wavelength for ICP/AES measurement should be 231.60 nm. If there is any interference from other elements, an alternative wavelength of 221.65 nm can be used.

ICP-MS is the most sensitive method to detect nickel at low ppt. X-ray methods are relatively less sensitive to AA or ICP/AES spectrometry but they do not require any acid digestion of the metal or its salts. They can be applied to solid powder for nondestructive measurement of the metal.

Toxicity

Skin contact can cause dermatitis and a type of chronic eczema, known as “nickel itch”, caused by hypersensitivity reactions of nickel on the skin (Patnaik, P. 1999. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 2nd ed. pp. 621-622, New York: John Wiley & Sons.) Although oral toxicity of the metal is very low, ingestion may cause hyperglycemia and depression of the central nervous system. Chronic inhalation of nickel dust can cause lung and sinus cancers in humans. Nickel and certain of its compounds are listed by IARC under Group 2B carcinogens as “possibly carcinogenic to humans” (*International Agency for Research on Cancer*. 1990. IARC Monograph, Vol. 49: Geneva.)

NICKEL ACETATE

[373-02-4]

Formula $(\text{CH}_3\text{COO})_2\text{Ni}$; MW 176.80; forms a stable tetrahydrate, $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ [6018-89-9].

Uses

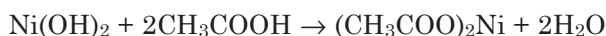
Nickel acetate is used as a catalyst. It also is used as a dye mordant in textiles. Other applications are in electroplating nickel and as a sealer for anodizing aluminum.

Physical Properties

The tetrahydrate is a green crystalline solid; sweet taste; odor of acetic acid; density 1.744 g/cm³; loses water on heating to form a yellow-green powder of anhydrous nickel acetate; decomposes above 250°C; soluble in water, 17g/100mL at 20°C; sparingly soluble in alcohol.

Preparation

Nickel acetate is prepared by reacting nickel hydroxide or nickel carbonate with dilute acetic acid. The tetrahydrate is crystallized from solution.



On heating, the solution hydrolyzes depositing nickel hydroxide.

Analysis

Elemental composition (of anhydrous acetate): Ni 33.21%, C 27.17%, H 3.42%, O 36.20%. The water of crystallization of the tetrahydrate may be determined by TGA and DTA methods. Nickel content of the salt may be determined by AA, ICP-AES and other instrumental techniques.

NICKEL ACETYLACETONATE

[3264-82-2]

Formula: $(\text{CH}_3\text{COCHCOCH}_3)_2\text{Ni}$; MW 256.93; monomeric in vapor phase but trimeric in solid phase; forms a dihydrate

Synonyms: bis(acetylacetonato)nickel(II); bis(2,4-pentanediono)nickel(II); bis(2,4-pentanedionato-O,O')nickel

Uses

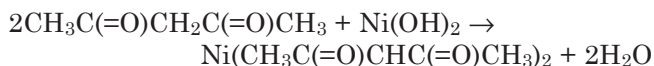
Nickel acetylacetonate is used as a catalyst in hydrogenation and other organic reactions.

Physical Properties

Emerald-green crystals; orthorhombic structure; density 1.455 g/cm³ at 17°C; melts at 230°C; soluble in water, alcohol, chloroform, benzene and toluene; insoluble in ether.

Preparation

Nickel acetylacetonate is prepared by the reaction of acetylacetone with nickel chloride hexahydrate or nickel hydroxide, followed by crystallization:



Analysis

Elemental composition: Ni 22.85%, C 46.75%, H 5.49%, O 24.91%. The compound may be characterized by its physical properties, elemental analysis, and by IR, UV and NMR spectra and x-ray diffraction data. A benzene or chloroform solution may be injected directly into a GC column and may be identified from its mass spectra. The characteristic mass ions for its identification by GC/MS are 58, 60, 100, 257. The aqueous solution or the nitric acid extract may be analyzed either by flame or furnace AA, or by ICP-AES to determine nickel content.